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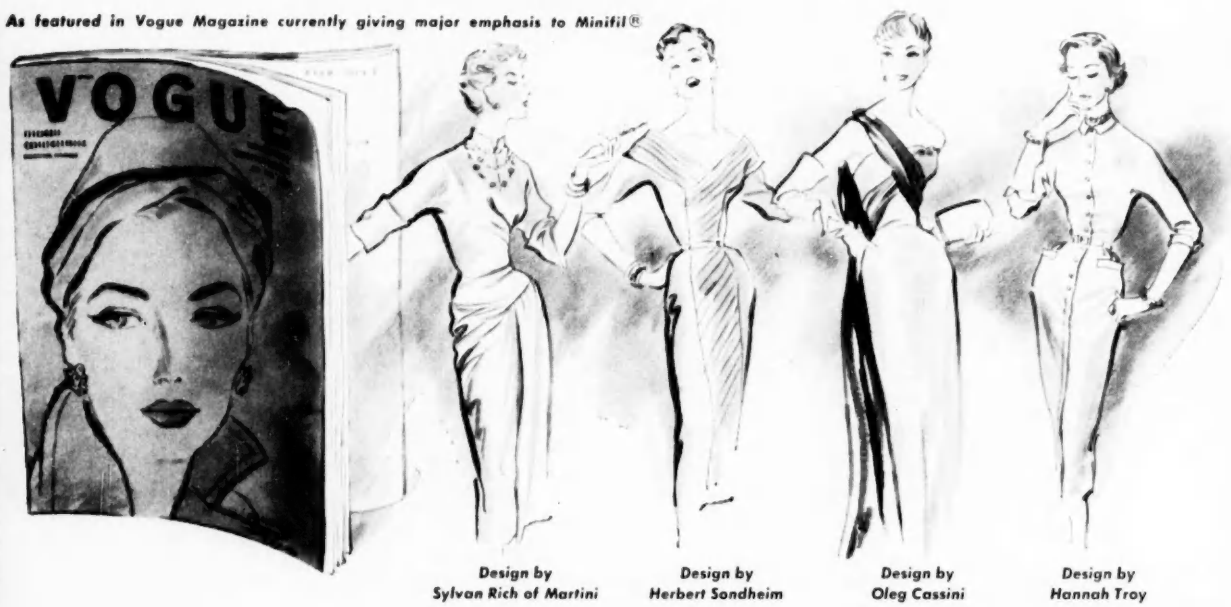

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VOL. XXIII, No. 9 September, 1953

In This Issue

Mechanical Behavior of Nylon Filaments in Torsion
W. G. Hammerle and D. J. Montgomery 595

Preparation of Microbiologically Resistant Wool by Means of Chemical Modification: Part I
Helmut Zahn and Hans Wilhelm 604

A Method of Preparing Bulk Cottons for Nep Counting
Priscilla L. Orcutt and Helmut Wakeham 614

Modification of Wool by the Application of Linear Synthetic Polyamides Part III: Pretreatment of Wool
D. L. C. Jackson 616

Measurement of Friction Between Single Fibers Part VII: Physicochemical Views of Interfiber Friction
Nils Gralén, Bertil Olofsson, and Joel Lindberg 623

Mechanical Properties of Cotton Fibers Part III: Effect of Alkali Hydroxide on Fibers Under Tension
E. L. Nimer, J. A. Lasater, and H. Eyring 629

Ethylenimine-Treated Cotton
George L. Drake, Jr., Wilson A. Reeves, and John D. Guthrie 639

Letters to the Editor
Supercontraction of Modified Keratin Fibers 642
A Device for Examination of Thickness of a Running Thread 643
Osmotic Active Substance of the Allwörden Reaction 645
Science Catches Up with an Industry 646

INDUSTRIAL SECTION

Frictional Properties of Filament Yarns and Staple Fibers as Determined by the Stick-Slip Method
G. W. Bartlett, T. M. Smith, and H. A. Thompson 647

Balloon Diameters and Thread Tensions Calculated for Different Cap-Spinning Conditions
J. Crank and Doreen D. Whitmore 657

Relationship of Fineness in Wool Top, Noil, Card Sliver, and Grease Wool
E. M. Pohle, D. D. Johnston, H. D. Ray, W. J. Manning, and W. A. Mueller 663

Book Reviews 671

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TEXTILE RESEARCH JOURNAL

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Mechanical Behavior of Nylon Filaments in Torsion*

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Abstract

The stress relaxation in torsion of 6,6-nylon filament is found to be nearly linear in the logarithm of time over periods from 20 to 20,000 sec. after twisting. On the basis of a generalized Maxwell model the behavior of the filament in free torsional vibration can be predicted from the results of the stress-relaxation experiments. The predictions were tested by experiments with a torsional pendulum whose period was varied from 50 to 400 sec. The angular displacement of the pendulum is an exponentially damped sinusoid over nearly the entire course of the motion. The observed dependence of the angular frequency upon the moment of inertia of the bob and the length of the filament agrees within 3% with the values predicted from the stress-relaxation experiments. The observed and predicted values of the damping constant agree within 13%. The stress relaxation in extension also is found to be nearly linear in the logarithm of time over periods from 10 to 2,000 sec. after stretching. Quantitative correlation between torsional properties and extensional properties has not been made because of the complications introduced by the anisotropy of the drawn nylon.

I. Introduction

The results of studies on the mechanical properties of high polymers are often described in terms of mechanical models, the models then being used to predict the results of new experiments. These models are based on combinations of Hookean springs (that is, springs whose restoring force is proportional to displacement) and Newtonian dashpots (that is, dashpots whose resisting force is proportional to velocity). In certain cases nonlinear force laws have been postulated, but as yet they have not proved very fruitful. A number of linear elements of the types cited are necessary to describe experiments of appreciable scope, and each element introduces a separate parameter. To keep the number of parameters manageably small, the number of elements must be small, or some law relating the parameters of the elements must be specified. It turns out that various series and parallel combinations of elements can be taken to describe the experimental results; unless there exists a molecular basis for preferring a given model, the particular combination chosen depends usually on the form of mathematics which conveniently describes the experiments of interest.

To determine the parameters of a specified model, one impresses some simple force or motion on the sample under study, and observes the behavior of the system with time or under variation of some parameter of the motion in case of steady-state response. Favorite types of experiments are: (*a*) forced sinusoidal vibration; (*b*) free vibration;

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(*c*) creep (motion under fixed load); (*d*) relaxation (force under fixed extension). For linear systems —that is, those obeying the superposition principle—each of these experiments is "complete" in the sense that the results from it determine the results of a general experiment in which any force or motion is impressed. In particular, the results from any one of the types of experiments listed must determine the results from all the others. A powerful check on the theory is available by comparing the results of two "complete" experiments of the type cited.

In the case of rubber, Kuhn and coworkers [2, 3, 4] correlated creep measurements with vibration measurements. Tobolsky, Dunell, and Andrews [5] studied the connection between relaxation and forced vibration for many elastomers, and found certain discrepancies between the forced-vibration response observed and that predicted on the basis of relaxation measurements. In these measurements the relaxation was observed over the interval of 10 to 1,000 sec. after extension of the sample, whereas the periods of the vibrations lay in the range of 0.01 to 1.0 sec.

It was believed likely that one source of the discrepancies was in the disparity of time scales for the two experiments, and that better agreement might be obtained by performing the vibrational experiments at periods of the same order as the time required for a substantial portion of the stress relaxation. Consequently, vibrational experiments on nylon, to be described in section III, were carried out with periods in the range of 50 to 400 sec. For experimental simplicity, free torsional vibrations were used instead of forced longitudinal vibrations. But if the torsional vibrations are to be compared with the extensional relaxation, some relationship must be postulated between the mechanical models applicable to extension and to torsion. To circumvent this difficulty, stress relaxation was observed in torsion (section II) as well as in extension (section VI). On the basis of a generalized Maxwell model it was found possible (section IV) to correlate the free vibrations in torsion with the stress relaxation in torsion. It was not found possible to correlate the stress relaxation in torsion with that in extension, at least not under the manifestly invalid assumption that the nylon is isotropic.

The method of prediction used in section IV involves a mathematical model consisting of an infinite parallel array of Hookean springs in series with Newtonian dashpots. A distribution function is used to describe the array. To see if one could use another generalization from the original Maxwell model of a single spring in series with a single dashpot, in section VII it was attempted to keep the number of elements equal to two, but to generalize the force law for the dissipative element by postulating that the resistive force is proportional to some time derivative of displacement other than the first. It is shown in this section that such a generalization is unsatisfactory.

II. Torsional Stress-Relaxation Experiments

The material used in these experiments was a drawn 6,6-nylon in the form of 30-den. (0.0024-in. diameter) continuous filament. The experiments were carried out in a room conditioned at 65% R.H. and 70°F. The top end of a 50-cm. length of the filament was cemented to a small mirror, which in turn was supported by a 10-cm. galvanometer suspension of 0.003-in. diameter gold filament rolled flat. The bottom end of the nylon was cemented to a cylindrical plastic bob weighing less than 10 g., from which projected radially a pair of steel pins at opposite ends of a diameter. The entire assembly was suspended from the top, with the bob pins riding freely between two pairs of upright stops mounted on the base of the support.

The nylon filament was twisted between 1 and 4 revolutions by rotating the stops by hand. After rotation, the filament was held at constant twist while the decaying torque was determined by meas-

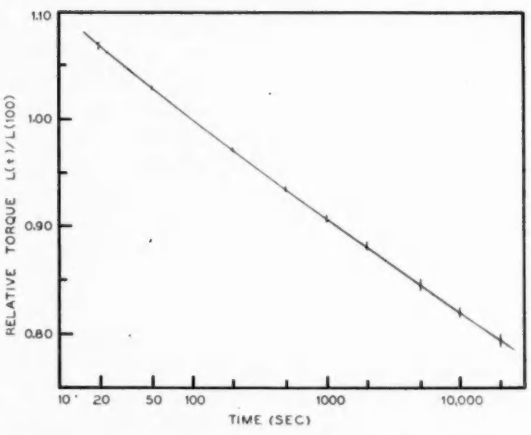

FIG. 1. *Average relative torque* L(t)/L(*100*) vs. *time* t *(logarithmic scale) for nylon filament in torsional relaxation.*

uring optically the angular position of the mirror. The torsional strain was kept essentially constant by making the mirror suspension strong enough in comparison with the nylon that rotation of the mirror was less than 0.003 revolution per revolution of the bob. The mirror suspension was calibrated for torque by measuring the change of the free-vibrational period of the suspension when a bob of known moment of inertia was suspended just below the mirror. To prevent the entire suspension from oscillating violently after twisting, a pair of small wires projecting from the mirror were placed as damping vanes in a cup of dibutyl phthalate. The proper amount of damping permitted measurement of the torque at times as short as 20 sec. after the initial rotation.

Figure 1 is a plot of the relative torque against time on a logarithmic scale. The relative torque is defined as the torque $L(t)$ at any time t seconds after rotation, divided by $L(100)$, the torque at 100 sec. The curve shown is an average curve of five separate determinations, the spread of the data being indicated by the short vertical lines on the curve. Within the experimental precision, $L(100)$ is proportional to the imposed twist, and the relative torque does not vary with the imposed twist. These relations show that the fiber behaves as a linear system at the strain levels of the experiment.

The average value of the torque $L(100)$ per unit twist for the five determinations is 10.08×10^{-3} dyne-cm./radian. This torque is composed of the resisting torque of the fiber itself plus the torque resulting from the raising of the bob against gravity when the fiber is shortened by twisting. The observed value of $L(100)$ must be decreased by about 10% to get the torque from the fiber alone. The average net torque is found to be 9.13×10^{-3} dyne-cm./radian at 100 sec. after twisting.

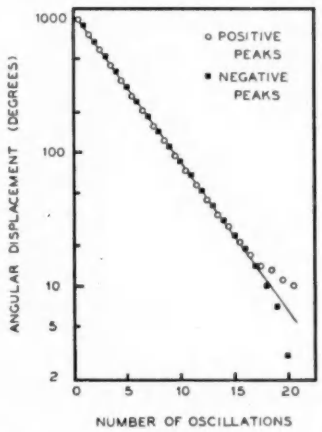

FIG. 2. *Maximum amplitude of angular displacement (logarithmic scale) vs. time (as measured in periods of oscillation) for a torsional pendulum supported by nylon filament.*

III. Torsional Free-Vibration Experiments

The materials and conditions for the free-vibration experiments were the same as those for the stress-relaxation experiments. A torsional pendulum was set up by hanging a cylindrical plastic bob from a length of nylon filament. The bob carried an angular scale on its periphery. The filament and bob were enclosed in a long glass tube to minimize effects of air currents. The pendulum was wound up by rotating the point of support, and was then released and allowed to rotate freely. The resulting angular displacement was observed through a low-power microscope, and the instants at which various scale divisions passed the microscope field were recorded on a chronograph. Both the length of the filament and the moment of the bob were changed in order to vary the rate of oscillation. The time required for a complete oscillation was between 50 and 400 sec., with filament length ranging from 5 to 100 cm. and bob moment of inertia equal to 7 or 20 g.-cm.^{2} The maximum twist during the experiment was 120°/cm. length of 30-den. nylon filament, corresponding to shear angles of less than 0.01 radian.

Within ½%, the time variation of the angular displacement, θ, throughout the course of the oscillations can be described by the following expression:

$$\theta(t) = \theta_o e^{-\alpha t} \cos \omega t, \qquad (1)$$

where θ_o = initial angular displacement from the equilibrium position (radians or degrees), α = damping constant determined from the data (sec.$^{-1}$), ω = angular frequency determined from the data (sec.$^{-1}$), and t = time (sec.) measured from instant of release of bob. The angular frequency is determined from the times when $\theta(t)$ crosses the time axis or from the intervals between the peaks in $\theta(t)$. The damping constant is determined from the slope of the graph of the peaks of $\theta(t)$ against t on a semi-logarithmic plot, as shown in Figure 2. The circles represent the greatest displacement at one end of the oscillation, the squares at the other. When the

maximum rotation during vibration becomes less than 10°, a small "creep" effect appears, and the exponential decrease is no longer followed. From the fact that no divergence from the exponential decrease occurs at rotations greater than 10° (1.0% of the initial displacement), it may be inferred that there exists no appreciable "sliding friction"—that is, frictional force opposed to the motion but independent of displacement or velocity.

When the moment of inertia, I, of the bob and the length, l, of the filament are changed, the angular frequency, ω, and the damping constant, α, change. Figure 3 shows the variation of ω with the product Il; the points are the experimental data, and the lines are the relations predicted from the stress-relaxation behavior in a fashion to be explained in the next section. Figure 4 shows the variation of α with Il; the points are the experimental data, and the lines are the predicted relations. The discrepancies between the predicted and observed values will be discussed later.

IV. Prediction of Free-Vibration Results from Stress-Relaxation Experiments

The dependence of α and ω upon Il in the torsional free-vibration experiments is predicted from the results of the torsional stress-relaxation experiments according to the following scheme:

A. A mechanical model is postulated to describe the fiber behavior, and the quantities characterizing it are determined from the relaxation experiment.

The mechanical model chosen is an infinite parallel set of Maxwell elements (Hookean spring in series with a Newtonian dashpot). The model is characterized by a distribution function $G'(\tau)$, where τ is the relaxation time of a given Maxwell unit. $G'(\tau)d\tau$ is the number of units having relaxation times between τ and $\tau + d\tau$.

If $G'(\tau)$ is known, then $L(t)$ can be calculated by the integral

$$L(t) = \int_0^\infty e^{-t/\tau} G'(\tau) d\tau. \tag{2}$$

In particular, if $G'(\tau)$ is given by

$$G'(\tau) = \begin{cases} 0 & \tau \leq \tau_{\min} \\ G_o/\tau & \tau_{\min} < \tau < \tau_{\max} \\ 0 & \tau \geq \tau_{\max} \end{cases} \tag{3}$$

where $\tau_{\min} \ll \tau_{\max}$, the stress relaxation will be linear in the logarithm of time, and will be equal to

$$L(t) \cong G_o(\ln \tau_{\max} - \gamma - \ln t) \tag{4}$$

for times much larger than $\tau_{\min}$ and much smaller than $\tau_{\max}$. Here γ is Euler's constant, 0.57722. The experimental stress relaxation shown in Figure 1 is nearly linear in $\ln t$, and $G'(\tau)$ is thus nearly equal to the box distribution defined by equation (3). If $L(t)$ is represented as a straight line tangent to the observed curve at 100 sec., the constant G_o is equal to 3.80×10^{-4} dyne-cm./ln sec., and $\tau_{\max}$ is equal to 4.7×10^{12} sec. This value of G_o is applicable only to the torsional behavior of a filament of the same radius and length as that used for the relaxation experiment.

B. Relations are postulated between the constants of the mechanical model and the dimensions of the filament.

A rigid material in the shape of a uniform circular cylinder of radius r and length l has a restoring torque L_G equal to

$$L_G = (\pi r^4 G/2l)\theta, \tag{5}$$

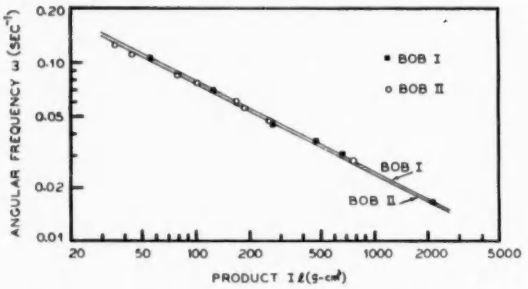

FIG. 3. *Logarithmic plot of angular frequency ω vs. product of moment of inertia I and length l for torsional pendulums supported by nylon filament (curves indicate predicted values, points indicate observed values).*

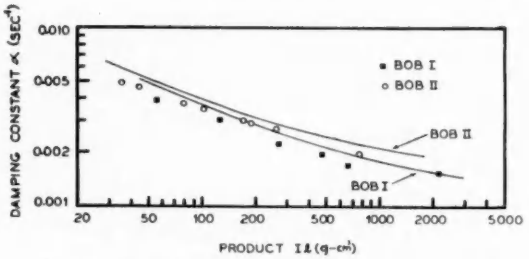

FIG. 4. *Logarithmic plot of damping constant α vs. product of moment of inertia I and length l for torsional pendulums supported by nylon filament (curves indicate predicted values, points indicate observed values).*

where G is the torsional modulus of the material and θ is the angle of twist. Similarly, a viscous fluid of the same geometry has a drag torque L_η equal to

$$L_\eta = (\pi r^4 \eta / 2l) d\theta/dt, \quad (6)$$

where η is the viscosity of the fluid and $d\theta/dt$ is the relative angular velocity of the end cross sections. It is assumed, of course, that there is no external drag between the fluid and the surrounding cylinder wall.

It will be assumed that similar relationships hold for all the springs and dashpots of the models. For any radius and length of filament, the box distribution will then have the magnitude

$$G'(\tau) = \pi r^4 G_o^o / 2l\tau, \quad (7)$$

where G_o^o is equal to 1.46×10^8 dyne/cm.^{2}-ln sec. when calculated from the slope of the relaxation curve at 100 sec. The value of τ_{max}, 4.7×10^{12} sec., will be independent of the filament dimensions.

C. The behavior of the mechanical model in free torsional vibration is calculated.

In the appendix are given the details of the calculation leading to the following implicit equations for ω and α as functions of Il:

$$\omega^2 - \alpha^2 = (\pi r^4 G_o^o / 2Il) \ln [\tau_{max} (\alpha^2 + \omega^2)^{\frac{1}{2}}], \quad (8)$$

$$\alpha\omega = (\pi r^4 G_o^o / 4Il)[\pi/2 + \tan^{-1} (\alpha/\omega)]. \quad (9)$$

These equations can be solved simultaneously for compatible values of ω and α corresponding to a specified value of the product Il, the computation being facilitated here by the smallness of the ratio α/ω.

The stress-relaxation curve is not exactly linear in the logarithm of time, and the actual behavior shown in Figure 1 must be approximated by a straight line, if equations (8) and (9) are to be employed. In the section below on possible sources of errors in the experiment, it will be shown that the best approximation to the relaxation curve when calculating a particular value of α and ω is the straight line tangent to the curve in Figure 1 at a time equal to $1/\omega$. The actual computation thus consists of selecting a value for ω, drawing the tangent at $t = 1/\omega$, determining the corresponding G_o^o and τ_{max}, and finally computing α and Il from equations (8) and (9).

D. Corrections are made for the lifting of the bob and for the damping from the air during free vibration.

The raising of the bob against gravity during twisting increases the vibrational frequency by a factor $(1 + mgA/\pi\omega^2 Il)^{\frac{1}{2}}$, where m is the mass of the bob, A is the cross-sectional area of the fiber, and g is the acceleration due to gravity. For bob I, this correction is about 10%; for bob II, about 5%. When α is considered as a function of Il, it also is changed by about the same percentages by the lifting action, inasmuch as the corrected ω is used to calculate α.

It is important to establish what part of the vibration damping arises from air friction, because this form of energy loss will not appear in the relaxation experiments. To determine the extent of the air damping, the same two bobs used in the free-vibration experiment were suspended from metal wires, in which the internal damping should be small. Figure 5 shows the damping constant for each of the two bobs as a function of the period of oscillation, which was varied by changing the wire length. For periods greater than 20 sec., α is independent of frequency, a result that would be expected if the damping were due entirely to the air drag on the bob. For shorter wire lengths and correspondingly shorter periods, the internal friction of the wire becomes important and the damping constant rises. The average values of the air damping at periods greater than 20 sec. are 0.00134 and 0.00098 sec.$^{-1}$ for bobs I and II, respectively.

If the motion of the air is laminar, and confined to a thin layer around the surface of the bob, the air damping is approximately proportional to the integral over the bob surface of the distance from the axis, divided by the moment of inertia. Evaluation of this quantity for the bobs gives about the

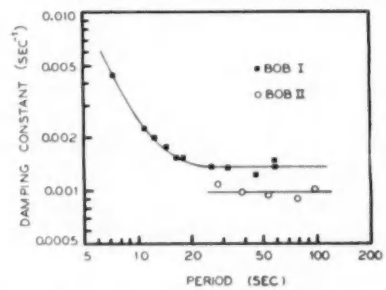

FIG. 5. *Logarithmic plot of air damping constant* vs. *period of oscillation for torsional pendulums supported by metal wire.*

correct ratio of the two observed damping coefficients, thereby lending credence to the idea that the damping at periods longer than 20 sec. is due almost entirely to the air and not to the wire. Hence, in the experiments with nylon filaments, it appears justifiable to add the values of the air damping determined above to the value of α calculated from equations (8) and (9) in order to obtain the total vibration damping. Presumably the frequency of the pendulum is altered so slightly by the air damping that no corresponding correction of ω is necessary.

After this final correction was made, the predicted values of α and ω were plotted in Figures 3 and 4, together with the experimental points. The experimental and predicted values of ω agree within 3% over the entire range of Il. The predicted and experimental values of α depend in the same way upon Il, but the predicted magnitude is high by 13%.

V. Sources of Discrepancy between Predicted and Observed Values

The box distribution of relaxation times defined by equation (3) does not exactly describe the stress relaxation shown in Figure 1, since the experimental results are not quite linear in the logarithm of time. If the predictions of ω and α as functions of Il are to be based upon a stress relaxation which is not linear in $\ln t$, some better estimate of $G'(\tau)$ than equation (3) is necessary. One such estimate [1] is based on the approximation that in the integral of equation (3) the factor $e^{-t/\tau}$ equals unity for all $\tau < t$, and zero for all $\tau > t$. Then

$$L(t) \cong \int_t^\infty G'(\tau)d\tau, \tag{10}$$

whence by differentiation

$$G'(\tau) \cong \frac{1}{\tau}\frac{dL(t)}{d\ln t}\bigg|_{t=\tau}. \tag{11}$$

In order to determine ω as a function of Il, the $G'(\tau)$ obtained from equation (11) is substituted into the integrand of equation (33) in the appendix and integrated over all τ. The integral of equation (33) may be evaluated by dividing the interval of integration into two parts at a time t' that is large compared with $1/\omega$ and small compared with τ_{max}. The integrand from $\tau = 0$ to $\tau = t'$ has its single maximum at a τ very close to $1/\omega$. Thus, from equation (11), the integral from zero to t' will not be much different from that for a box distribution corresponding to a relaxation which follows the straight line tangent to $L(t)$ at $t = 1/\omega$. The integral from $\tau = t'$ to $\tau = \infty$ is nearly equal to $L(t')$, as given by equation (10), since the coefficient of $G'(\tau)$ in equation (33) approaches unity at large τ. Because the box distribution just mentioned predicts a value for $L(t')$ not much different from its actual value (the tangent at $t = 1/\omega$ lying only slightly below $L(t)$ at large t), it is possible to evaluate the entire integral by the corresponding box distribution. In this way, the graphical differentiation involved in equation (11) is obviated, and equation (9) may be used to find a value of ω that is not expected to be much in error.

To find α as a function of Il, the $G'(\tau)$ obtained from equation (11) is substituted into the integrand of equation (34) in the appendix and integrated graphically over τ. There is no simple approximating method for evaluation of the integral, because as τ becomes very large the integrand approaches $G'(\tau)/\tau$ and not $G'(\tau)$. That is to say, α is sensitive to properties of $L(t)$ besides its magnitude and slope at $t = 1/\omega$. A graphical integration to find α, carried out for $\omega = 0.02$, predicts a value of α within 2% of the value obtained from substitution of the corresponding box distribution into equations (8) and (9). Because the graphical integration involves extrapolation of $\tau G'(\tau)$ back to $\tau = 0$ from $\tau = 20$ sec., it probably contains errors at least as large as 2%. Consequently, it was not considered worth while to perform graphical integrations for other values of ω. All in all, errors of several percent in the prediction of the free-vibration experiments from the relaxation experiments are to be expected as a result of approximations in the specification of the distributions and in the evaluation of the integrals.

In the analysis of the free-vibration experiments, the assumption is made that the effect of creep during free vibration is small. This assumption seems tenable in view of the small deviation of the observed behavior from a damped sinusoid.

Two separate calibrations of the stress-relaxation apparatus agree to within 2%, and it is believed that the experimental spread occurring in repeated stress-relaxation runs is due to variation in the filament diameter and strength. This belief is supported by the amount of variation in the cross-sectional area as measured vibroscopically. Two 1-in. samples taken adjacent along the fiber agree in area to within 2%, but samples taken several feet apart

vary by as much as 4%. The torsional modulus of the fiber is dependent upon the square of the area, and thus may vary by about 8%. The maximum observed variation in the ratio of $L(100)$ to impressed twist is 5% in five stress-relaxation runs, and is consistent with the observed area variation.

The values of the time corresponding to the experimental values of $1/\omega$ are as low as 10 sec. To evaluate $G'(\tau)$ at these low times, the curve of $L(t)$ *versus* $\ln t$ must be extrapolated back from 20 sec. Error of several percent in the predicted values of ω and α may arise from the extrapolation.

In summary, the variation of the cross section of the fiber can more than account for the experimental variation of ω and α at constant Il; and the difference between predicted and observed values does not exceed the probable accuracy of the calculations.

VI. Extensional Stress-Relaxation Experiments

Previous investigators [5] of nylon worked with strains in extension. The measurement of extensional stress relaxation was repeated here in order to see what correlation might be possible between the extensional and torsional constants of nylon. The same material under the same conditions of temperature and relative humidity was used in both the extension and torsion experiments. An Instron tensile testing machine was used to extend a 2-in. gage length of nylon filament to a strain of 1%, 2%, or 5%. The filament was held at fixed extension while the decaying force was recorded automatically over a period of 2,000 sec. At each total extension the rate of strain was varied to provide extension times ranging from 1 to about 10 sec.

Figure 6 is a plot of the relative force against time on a logarithmic scale. The relative force is defined as the force $F(t)$ at any time t seconds after completion of the extension, divided by $F(100)$, the force at 100 sec. The average curve for six different relaxations at 1% or 2% extension is shown, the vertical lines on the curve indicating the spread in the runs. The spread may be ascribed primarily to small variations with time in the temperature and relative humidity of the controlled atmosphere, and to zero shift in the apparatus measuring the force. For 1% and 2% extensions, $F(100)$ is proportional to the extension, and the relative force does not change in its dependence upon time. With 5% extension, for which the results are not shown, the relative force curve retains the same general shape but is steeper. From this change in slope it may be concluded that the filament behaves as a linear system up to 2% extension, but not at 5%.

The downward concavity of the curve at small times is probably attributable to the finite time required for extension, because the concavity becomes more pronounced as the rate of extension decreases. Beyond 10 sec. after extension, the curve is independent of the rate of extension, and is perhaps slightly concave upward, like the torsional relaxation curve in Figure 1. The analytical expression for the straight line tangent to the curve at 100 sec. is

$$F(t)/F(100) = 1 - 0.0570 \ln (t/100). \quad (12)$$

In terms of stress this equation becomes

$$s(t)/s_o(100) = \epsilon[1 - 0.0570 \ln (t/100)], \quad (13)$$

where $s(t)$ is the stress at time t, $s_o(100)$ is the stress at 100 sec. per unit extension, and ϵ is the strain. The value of $s_o(100)$, computed by dividing the force by the cross-sectional area, is 2.23×10^{10} dynes/cm.^{2}

The stress relaxation may be described approximately by the same sort of box distribution of relaxation times as was used in the torsion experiments (*cf.* equation (3)). The distribution (with obvious notation) corresponding to the tangent to the relaxation curve at 100 sec. is

$$E'(\tau) = \begin{cases} 0 & \tau \leq \tau_{\min} \\ E_o^o/\tau & \tau_{\min} < \tau < \tau_{\max} \\ 0 & \tau \geq \tau_{\max} \end{cases} \quad (14)$$

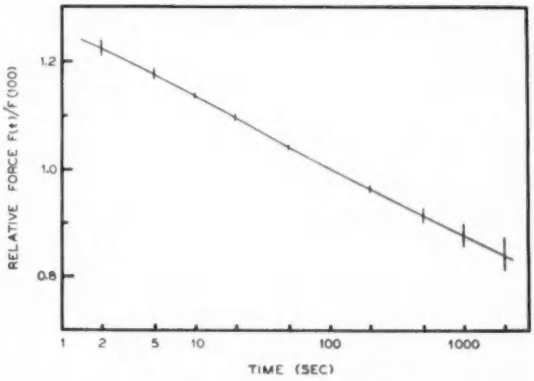

FIG. 6. *Average relative force* F(t)/F(*100*) vs. *time* t *(logarithmic scale) for nylon filament in extensional relaxation.*

where $E_o^o = 1.27 \times 10^9$ dynes/cm.^{2}-ln sec., $\tau_{max} = 7.4 \times 10^9$ sec., and $\tau_{min} \ll 10$ sec. This distribution of relaxation times may be used to predict the result of any general extension experiment, but some additional assumptions about the nylon must be made before the distribution can be applied to torsion experiments. If it is assumed that the shear modulus $G'(\tau)$ of any element of the model is related to its extension modulus $E'(\tau)$ in the same way as for a rigid isotropic material, then

$$G'(\tau) = E'(\tau)/2(1 + \sigma), \qquad (15)$$

where σ, Poisson's ratio, is not very far from 1/2 for nylon. If it is further assumed that the same relationship holds between the extensional solid viscosity and the shear solid viscosity, the distribution function describing the fiber in torsion will be a box with τ_{max} the same as for extension. For $\sigma = 1/2$, the predicted value for G_o^o is 4.22×10^8 dynes/cm.^{2}-ln sec., and for τ_{max} is 7.4×10^9 sec. Such a value of G_o^o is higher by a factor of 2.9 than the value determined from the slope of the torsional relaxation curve at 100 sec. The value of ln τ_{max} is lower by a factor of 0.78. These discrepancies are far outside the experimental error, and it is concluded that the torsional relaxation cannot be correlated with the extensional relaxation on the preceding assumptions.

Another possible set of assumptions would be to relate the elastic moduli as before, but to keep the solid viscosities of the elements the same for torsion as for extension. If $\sigma = 1/2$, the box distribution for torsion would then have $G_o^o = E_o^o = 1.27 \times 10^9$ dynes/cm.^{2}-ln sec., with $\tau_{max} = 2.2 \times 10^{10}$ sec. This value of G_o^o is 8.7 times higher than the value determined from the slope of the torsional relaxation curve at 100 sec. It is apparent that neither set of assumptions correctly describes the relationship between extension and torsion.

This discordance is hardly surprising, for it is well known from x-ray diffraction and other evidence that drawn nylon is not isotropic, but rather that the molecular chains in the crystalline regions of the material are preferentially oriented parallel to the fiber axis. If the crystalline material is stronger than the amorphous material, the torsional modulus should be lower than the value predicted from the extensional modulus by use of equation (15). This expectation is confirmed in the experiments just described; indeed, this type of experiment may furnish a tool for examination of anisotropy in fibrous materials.

VII. Attempt to Generalize the Viscous Law in a Voigt Model

Examination of equations (8) and (9) shows that α is proportional to ω when $\alpha/\omega \ll 1$. The simplicity of this relation suggests a search for a simple Voigt model with only two parameters—a spring in parallel with a dashpot—but with a generalization of the law for the damping force in the dashpot. To retain the feature of linearity and thus be able to make use of the principle of superposition, the force is restricted to be a linear differential or integral operator.

The damped sinusoidal wave of equation (1) may be regarded as the solution of any one of an arbitrary number of differential equations. For physical reasons, one likes to consider a differential, or integrodifferential, equation of the following form, linear in θ:

$$d^2\theta/dt^2 + 2\alpha[\text{damping term}] + \omega_o^2(1 + \epsilon_o)\theta = 0, \qquad (16)$$

where the quantity within brackets describes the damping. The quantity ϵ_o is small, of the order of α^2/ω^2. It may be shown that substitution of equation (1) into equation (16) gives:

$$d^2\theta/dt^2 + 2\alpha(1 + \epsilon_1)\omega^{1-m}\theta^{(m)} + \omega^2(1 + \epsilon_o)\theta = 0, \qquad (17)$$

where ϵ_o, ϵ_1 = small quantities of order of α^2/ω^2, m = odd* integer, and $\theta^{(m)}$ = mth derivative (integral) of θ, for positive (negative) m. For the special case of $m = 1$, it turns out that $\epsilon_o = \alpha^2/\omega^2$, $\epsilon_1 = 0$.

Suppose the resistive force of the dashpot in the model is proportional not necessarily to the first derivative of the displacement but to $\theta^{(m)}$, the m th derivative of the displacement, with the proportionality constant η_m; then the following relation may be shown to be the equation of motion for a torsional pendulum supported by a filament whose mechanical equivalent is a Hookean spring in parallel with a dashpot of the type just described:

$$Id^2\theta/dt^2 + (\pi r^4\eta_m/2l)\theta^{(m)} + (\pi r^4 G/2l)\theta = 0. \qquad (18)$$

For the special case of $m = 1$, the damping term

* Even values of m do not lead to an equation parallel with equation (16) where the coefficients are real.

represents ordinary Newtonian damping, with $\theta^{(m)} = d\theta/dt$, and $\eta_m = \eta$, the ordinary solid viscosity.

Comparison of equation (18) with equation (17) leads to the following approximate associations:

$$2\alpha\omega^{1-m} \sim \pi r^4\eta_m/2Il, \quad (m \text{ odd}) \tag{19}$$

$$\omega^2 \sim \pi r^4 G/2Il, \tag{20}$$

which, upon elimination of Il and fixing of r, η_m, and G, lead to

$$\textit{Predicted:} \qquad \alpha \sim \omega^{m+1} \quad (m \text{ odd}). \tag{21}$$

(For the special case of $m = 1$, $\alpha \sim \omega^2$ on this model.) But the observed dependence of α on ω is

$$\textit{Observed:} \qquad \alpha \sim \omega^1. \tag{22}$$

Thus, there exists no odd value of m, either positive or negative, which will permit reconciliation of the observed values with those predicted by use of the generalized Voigt-type model.

VIII. Summary

For 30-den. drawn nylon filaments subjected to extensions not exceeding 2% or twists not exceeding 120°/cm., at 70°F and 65% R.H., it has been found that:

(*a*) The time variation of the torque on a filament held at fixed twist is linear in the logarithm of time between 20 and 20,000 sec., except for a slight concavity upwards.

(*b*) The time variation of the angular displacement of a freely oscillating torsional pendulum supported by the filament is an exponentially damped sinusoid over the entire course of the motion, except at very long times.

(*c*) From the behavior of the filament in torsional relaxation, its behavior in free torsional vibration can be predicted within about 3% with respect to frequency, and within about 13% with respect to damping constant.

(*d*) The time variation of the stretching force on a filament held at fixed extension is nearly linear in the logarithm of time, except possibly at very short and very long times.

(*e*) The course of the extensional relaxation fails to predict the course of the torsional relaxation under the assumption that the nylon filament is mechanically isotropic.

(*f*) A Maxwell-type linear two-element model cannot satisfactorily represent the filament behavior, even when the force law for the dissipative element is generalized to admit time derivatives other than the first, the spring being kept Hookean.

Appendix

Each element of the chosen model consists of a spring of strength $G'(\tau)$ in series with a dashpot of viscosity $\tau G'(\tau)$. The displacement $\theta(t)$ will be equal to $\theta_1(t)$, the displacement of the spring, plus $\theta_2(t)$, the displacement of the dashpot:

$$\theta(t) = \theta_1(t) + \theta_2(t). \tag{23}$$

Now θ_1 and θ_2 will be related to the torque $L_\tau(t)$ on the element by

$$L_\tau(t) = G'(\tau)\theta_1(t), \tag{24}$$

$$L_\tau(t) = \tau G'(\tau)d\theta_2(t)/dt. \tag{25}$$

These three equations yield the following relation between L_τ and θ:

$$\tau dL_\tau(t)/dt + L_\tau(t) = \tau G'(\tau)d\theta(t)/dt. \tag{26}$$

If, for free vibration, one assumes that

$$\theta(t) = \theta_o e^{-\alpha t}\cos\omega t, \tag{27}$$

the particular solution* of equation (26) is found to be

$$L_\tau(t) = \frac{\theta_o G'(\tau)e^{-\alpha\tau}}{\omega^2\tau^2 + (\alpha\tau - 1)^2} \times \{[\tau^2(\omega^2 + \alpha^2) - \alpha\tau]\cos\omega t - \omega\tau\sin\omega t\}. \tag{28}$$

The total torque $L(t)$ on the entire distribution of elements will be

$$L(t) = \int_o^\infty L_\tau(t)d\tau, \tag{29}$$

or

$$L(t) = e^{-\alpha t}(A\cos\omega t + B\sin\omega t), \tag{30}$$

where A and B, obtained by substitution of $L_\tau(t)$ from equation (28) into equation (29), are independent of the time. But this torque must also be equal to the torque on the fiber due to the motion of the bob with moment of inertia I:

$$L(t) = -Id^2\theta(t)/dt^2, \tag{31}$$

* The general solution of equation (26) contains, in addition, a term which decreases monotonically in time, and which represents a small creep superimposed on the free vibration. Within the precision of the experiments, this term may be neglected.

which, in conjunction with equation (27), gives

$$L(t) = I\theta_0 e^{-\alpha t}[(\omega^2 - \alpha^2)\cos\omega t - 2\alpha\omega \sin\omega t]. \quad (32)$$

Since equations (30) and (32) are valid for all values of the time, the coefficients of their sine and cosine terms may be equated separately, to give

$$I(\omega^2 - \alpha^2) = \int_0^\infty \frac{[(\omega^2 + \alpha^2)\tau^2 - \alpha\tau]G'(\tau)}{\omega^2\tau^2 + (\alpha\tau - 1)^2}\, d\tau, \quad (33)$$

and

$$2\alpha I = \int_0^\infty \frac{\tau G'(\tau)}{\omega^2\tau^2 + (\alpha\tau - 1)^2}\, d\tau. \quad (34)$$

These integrals may be evaluated if the distribution $G'(\tau)$ is known from the stress relaxation. Equations (8) and (9) result when $G'(\tau)$ is given by equation (3), and when it is assumed that both $1/\omega$ and $1/\alpha$ are much larger than τ_{min}.

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Preparation of Microbiologically Resistant Wool by Means of Chemical Modification: Part I*

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Introduction

The microbiological degradation of fibers—*i.e.*, their destruction by bacteria and fungi—is a well-known phenomenon observed when a suitable fiber substrate is exposed to the action of active organisms under biologically favorable conditions (pH, temperature, moisture, atmosphere). For economic reasons, however, as compared to wool fibers, the microbiology of the cellulose fibers and their protection have received much more detailed attention.

Since it is not here proposed to append a complete list of all the literature on the microbiology of wool since the appearance of the first scientific work by W. Kalman (*Lehnes Färber-Ztg.*, pp. 245, 377 (1902)), reference is made to a few papers in which the field is critically surveyed and summarized. The most important of these are: "Mikrobiologie der Wolle" by H. Glafey, D. Krüger, and G. Ulrich in Herzog's "Technologie der Textilfasern," Vol. VIII, 3B ("Technologie der Wolle," Berlin, Springer Verlag, 1938), p. 107; "Problems in the Microbiology of Protein Fibres," by E. Race, in "Symposium on Fibrous Proteins," Leeds, England, Soc. Dyers and Colourists, 1946, p. 80; "The Mildewing of Wool, Causes and Prevention," in *Wool Science Review* **6**, 32 (1950). Papers from recent German literature by Nopitsch [17] and Wegener [24] should also be mentioned here. From the papers cited we are able to infer the state of present-day knowledge concerning, *inter alia*, the following questions of microbiological importance: Which bacteria and fungi are capable of attacking wool? Which pretreatments of wool and

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which impurities favor microbiological degradation? At what moisture content, temperature, pH, and redox potential are the various bacteria and fungi the most dangerous for wool? In which stages of wool manufacture can microbiological damage make its appearance? Which fungicides and bactericides afford temporary protection during manufacture, and what degree of stability can be achieved against washing and dry-cleaning?

The present authors carried out research with the object of establishing the feasibility of protecting wool against attack by bacteria and fungi by means of chemical modification—*i.e.*, by introducing additional groups into the wool proteins, these groups being bound covalently (substitution), or by replacement of groups in the proteins with residues of a different type.

Experiments of this type were first carried out on wool by Harris and his coworkers. Wool reduced with thioglycolates and treated with organic halogen derivatives proved to be stable to enzymes [9]. However, our attention was first drawn to the full implications of the method by various publications in the American literature. Thus, Goldthwait [11] succeeded in preparing bacteria-resistant cotton by chemical modification—*i.e.*, by joining the macromolecular chains with well-defined chemical compounds by main valency bonds. For example, acetylated cotton (acetyl content, 20%–30%) and formalized cotton (CH_2O content, 1.3%) proved to be largely resistant to bacterial and fungous attack in the soil-burial test.

Conversion of the cellulose into its ether is also effective (45.8% ethoxy-group content, which corresponds to $\frac{2}{3}$ of the hydroxyls methylated) [12].

Since, according to Siu [22], the actual substituents introduced into the cellulose molecule are immaterial so far as the effectiveness of the chemical modification is concerned, such modifications as confer desirable properties other than resistance to microorganisms, such as incombustibility, photochemical stability, and water repulsion, are preserved.

A valuable indication for further investigation was provided by experiments carried out by Zahn and Würz [26] on dinitrophenylated silk, whose moisture adsorption was found to be strongly reduced. A certain "desiccation" of the cotton fibers as a result of reduction in swelling is, according to experiments carried out by Goldthwait, Buras, and Cooper [10], the real cause for resistance of acetylated and formalized cotton to fungous attack.

Numerous papers (Speakman, Harris, Kirst, Elöd, Hartmann [25], Rath [20]) describing methods employed for the chemical modification of wool have appeared.

Several of the methods described for the chemical modification of wool were tested for application to the preparation of microbiologically resistant wool. Real biological tests, such as resistance of the chemically modified wool sample to pure cultures of bacteria and fungi, were not carried out. Rather, stress was laid on investigation of the prerequisites of permanent fiber protection by means of chemical modification and on the relationship between constitution and microbiology of wool. We therefore satisfied ourselves with the experimentally simple burial and rotting tests for comparison with untreated wool. We were then able to judge the effectiveness of chemical modification by numerical evaluation of the resistance to tearing of the buried yarn. We considered it important to place our investigations on a numerical basis in this manner.

Description of Experiments

Wool

All experiments were carried out with raw white noncarbonized Sportgarn * of spin no. $11\frac{1}{2}/4$. Twelve-meter lengths of yarn were cut up into strands of 25 cm. length. These were washed with 0.5% Nekanil † solution (standardized to pH 4 with acetic acid) and then with distilled water, and were finally dried in air. The pH value of the yarn purified in this manner (determined by heating 1 g. of yarn with 30 cc. of water at 90°C for 1 hr., the pH then being measured in an ionometer ‡) was found to lie between 4.5 and 5.5.

Chemical Modification of Wool Yarn by Reaction with Monofunctional Compounds

(1) Esterification with methanol [3].—The yarn was treated in the ratio 1 : 50 with $N/10$ hydrochloric acid in methanol for 6 days at room temperature. The sample was then filtered at the pump, washed

* We are indebted to the firm Schachenmayr, Mann & Cie., Salach/Württemberg, Germany, for kindly placing this at our disposal.

† B.A.S.F. (Badische Anilin- und Sodafabrik), Ludwigshafen, Germany.

‡ L. Pusl, München, Germany.

with methanol and water, neutralized by soaking in water brought to pH 8 with NH_3, and finally washed once again and dried in the air.

(*2*) *Esterification with epichlorohydrin according to Alexander's method* [*1*].—The yarn was treated with a 5% aqueous epichlorohydrin † solution in the ratio 1:30 for 2 hrs. at 95°C, sucked at the pump, carefully washed, and finally purified and dried as described in (*1*).

(*3*) *Acetylation* [*4*].—The wool was boiled under reflux for 30 min. with freshly distilled acetic anhydride in the ratio 1:50. The yarn, whose color had changed to brown, was filtered at the pump, washed with distilled water, and dried in the air.

(*4*) *Dinitrophenylation* [*8*].—Ten grams of wool was loosely wound around a propeller stirrer, which was then placed in a vessel containing 7 g. of sodium bicarbonate dissolved in 160 cc. of water. Five grams of dinitrofluorobenzene [*27*]dissolved in 480 cc. of alcohol was then added to the soda solution. The mixture was allowed to react for 14 hrs. at 40°C with continuous stirring (200 r.p.m.). The final pH value was found to be 8.25. The yellow dyed yarn was sucked dry, thoroughly washed with distilled water, soaked in water brought to pH 4 with acetic acid, and then rewashed and dried in the air.

(*5*) *Nitration.*—Ten grams of wool was treated with 750 cc. of 1 vol. % HNO_3 for 3 hrs. on the boiling water bath. The red-brown colored yarn was then washed with water, brought to pH 5, and dried.

Chemical Modification of Wool Yarn by Reaction at the Cystine Disulfide Bond

(*1*) *HS-wool.*—Ten grams of wool was treated with a solution of 5.55 g. of thioglycolic acid and 2.15 g. of $Ca(OH)_2$ in 300 cc. of water for 3 hrs. at 50°C, then washed with ice water until no further thiol reaction was obtained (with $FeCl_3$), and finally dried in the air.

(*2*) *CH_3-S-wool.*—The preparation of wool with built-in S-methyl cystein groups was achieved by methylation of the reduced HS-wool (*cf.* (*1*)) with a solution of 7.5 g. of methyl iodide and 2.5 g. of sodium bicarbonate in a mixture of 250 cc. of acetone and 50 cc. of water. The reduced yarn was boiled with this solution under reflux until the nitroprusside-sodium reaction for free SH groups in the fiber was negative. The sample was then thoroughly washed with dilute acetic acid and acetone.

† Kindly provided by B.A.S.F.

(*3*) *Ethylene*-bis-*cystein-wool* [*19*].—Ten grams of HS-wool (*cf.* (*1*)) was treated with a solution of 5 g. of 1,2-dibromoethane and 2.5 g. of bicarbonate in 250 cc. of acetone and 50 cc. of water for 4 hrs. under reflux. The sample was then pressed out, washed with water rendered weakly acidic with acetic acid, and finally washed with acetone.

Chemical Modification of Wool Yarn by Reaction with Bifunctional Compounds

(*1*) *Reaction with 4,6-*(bis-*chloromethyl*)-*1,3-dimethylbenzene* * *according to the method of Kirst* [*15*].—Ten grams of wool was heated with a solution of 2.12 g. of the above compound and 2.5 g. of sodium bicarbonate in 250 cc. of acetone and 50 cc. of water for 5 hrs. under reflux. The sample was then drained and washed with 3,000 cc. of water. After 24 hrs. the pH was found to be 8.4. This was brought to pH 5 with acetic acid.

(*2*) *Blank test without 4,6-*(bis-*chloromethyl*)-*1,3-dimethylbenzene.*—Ten grams of wool was treated as described in (*1*), the only difference being the omission of the dichloro compound.

(*3*) *Formalization.*—Ten grams of wool was boiled with 500 cc. of 2% formaldehyde solution in *N*/20 H_2SO_4 for 2 hrs. under reflux. The sample was then washed with distilled water and brought to pH 5 with NH_3.

(*4*) *Blank test without formaldehyde.*—Ten grams of wool was boiled with 500 cc. of *N* 20 H_2SO_4 under reflux.

(*5*) *Reaction with butandiol*-bis-*chloromethyl ether* (*Kirst's method* [*16*]).—Ten grams of wool was treated with a solution of 1 g. of butandiol-*bis*-chloromethyl ether (Höchst) and 0.5 g. of pyridine in 330 cc. of carbon tetrachloride at 50°–55°C for 3 hrs. After draining, the sample was washed thoroughly with 3 liters of distilled water (pH after 24 hrs., 2.5). The pH was brought to 5 with acetate buffer.

(*6*) *Blank test without butandiol*-bis-*chloromethyl ether.*—Ten grams of wool was treated with a solution of 0.5 g. of pyridine in 330 cc. of carbon tetrachloride at 50°–55°C for 3 hrs.

(*7*) *Reaction with Kaurit 140* † *according to the method of Hartmann* [*14*].—Eighty grams of Kaurit 140 and 4 g. of ammonium nitrate were dissolved in

* Kindly provided by Farbwerke Höchst.

† Kaurit 140 is tetramethylol-acetylen-diurea (from B.A.S.F.).

1,000 cc. of water. Ten grams of wool was treated with 300 cc. of this solution for 1 hr. at room temperature, and then centrifuged and heated to 130°C for ½ hr.

Changes in Wool Yarn Brought About by Other Reagents

(*1*) *Reaction with potassium cyanide solution.*—Ten grams of wool was treated with 500 cc. of 0.1*M* potassium cyanide solution for 16.5 hrs. at 66°C.

(*2*) *Reaction with caustic soda.*—Ten grams of wool was treated with 500 cc. of *N*/100 caustic soda for 16.5 hrs. at 66°C.

(*3*) *Chlorination.*—Ten grams of wool was treated with 300 cc. of sodium hypochlorite solution (1 g. active chlorine per liter) for 10 min. at 15°C. Excess chlorine was subsequently removed with $NaHSO_3$ (4% soln., R.T., 10 min.).

(*4*) *Alcoholic potash* [*5*].—Ten grams of wool was treated with 1,000 cc. of a 2% solution of KOH in 95% ethanol for 15 min. at 22°C. After pressing out, the sample was treated with 0.2*N* sulfuric acid for 10 min. and washed.

(*5*) *Dry heat.*—Ten grams of wool yarn was heated for 24 hrs. at 130°C in a Heraeus drying oven.

Treatment of Wool with Various Reagents which Do Not Enter into Permanent Combination with the Fiber

(*1*) Ten grams of wool was boiled for 1 hr. with 300 cc. of a solution of 2.5 g. of Eulan neu * and 1 g. of conc. H_2SO_4 in 750 cc. of water. The final pH value was 2.25.

(*2*) The wool was boiled for 1 hr. with 4% of its weight of sulfuric acid in the ratio 1 : 30.

(*3*) Ten grams of wool was treated with 300 cc. of a 1% solution of 2,4,5-trichlorophenol † in alcohol for 5 hrs. at 20°C and then freed from solution in the centrifuge.

(*4*) Wool was treated with 1% 2,4,5,6-tetrachlorophenol solution in the ratio 1 : 30 for 5 hrs. at 20°C.

(*5*) Wool was treated with 1% pentachlorophenol solution in alcohol in the ratio of 1 : 30 for 5 hrs. at 20°C.

* Bayer, Leverkusen, Germany.

† Kindly provided by B.A.S.F.

Testing Methods

(*1*) *Soil-burial test.*—For testing the resistance of the treated wool against bacteria and fungi in the soil-burial test, five small skeins, each weighing 2 g., were used. Five ordinary flower pots (diameter at top, 13 cm.) were half-filled with good garden soil.

The soil was prepared from foliage, vegetable refuse, and grass. Liquid and artificial manures were not added, but a little lime was mixed in. A rotting period of 3 years was allowed, during which time no plants grew on the earth (with the exception of a few weeds).

The five skeins were placed separately in the pots, covered with soil, and pressed firm. Each flower pot was sprinkled with 30 cc. of water every 24 hrs. Fifteen liters of distilled water was poured onto 1 kg. of soil, the upper liquid layer being used for watering. The temperature in the test room was maintained at 20° ± 1°C. The relative humidity fluctuated between 60% and 80%.

Five flower pots were necessary for each method of treating the wool. The investigation of a series of up to ten different samples (fifty pots) presented no particular difficulty. Five untreated yarn skeins were run in each series for purposes of comparison. The aqueous solution squeezed out from the soil and decayed untreated wool after 14 days were found to have a pH of 8.6. The separate skeins were dug out after 5, 10, 15, 20, and 25 days, respectively, freed mechanically from adhering earth, rinsed with Leonil O, washed, and finally dried in the air.

(*2*) *Tensile strength and elongation at rupture.*—The dry tensile strength and dry elongation at rupture of the unearthed yarn were measured in a simple wool resistance tester.* The length of strand stretched was reduced to 250 mm. Ten measurements were made for each sample. The algebraic means of the tensile strength and the elongation at rupture were plotted as ordinates against the burial period of the respective sample as abscissa. From the graph obtained, the so-called "half-life period" of the yarn was ascertained. This represents the number of days which the earth requires to reduce the dry tensile strength of the yarn to 50% of its initial value.

(*3*) *Alkali solubility* [*13, 28*].—Wool weighing 400 mg. was dried in a weighing glass in a Heraeus drying oven for 8 hrs. at 105°C; the weighing glass

* Frank, Weinheim, Germany.

was then closed and transferred to a desiccator, where it was allowed to cool for 30 min. Meanwhile a number of test tubes, 3 cm. × 20 cm., were each filled with 40 cc. of $N/10$ NAOH and heated to 65°C in the Höppler thermostat. As soon as the temperature had become steady, the dried wool samples were introduced into the tubes and allowed to react with the $N/10$ NaOH for exactly 60 min., with frequent shaking. The caustic soda was then decanted off, and the samples were washed thoroughly with distilled water and sucked dry on sintered glass, G1 or G2. They were then placed in dilute acetic acid solution (pH 4), and after 12–24 hrs. once again sucked dry, dried in a weighing glass for 8 hrs. at 105°C, and finally weighed after another hour. Alkali solubility = percentage loss in weight of the wool sample after completion of the treatment described.

(*4*) *Acid solubility* [*28*].—Samples of wool yarn weighing 400 mg. each were treated as described under (*3*). Instead of $N/10$ caustic soda, however, the wool was submitted to the action of $4N$ hydrochloric acid for 60 min. at 65°C. After completion of the reaction, the sample was placed in very dilute ammonia (pH 8) instead of in acetic acid.

(*5*) *Supercontraction of wool in 50% phenol solution.*—This testing method was described elsewhere by one of the present authors (Zahn, H., *Textil-Praxis* **1950**, p. 315) .

(*6*) *Cystine analysis* [*21*].—Samples of wool yarn weighing 200–230 mg. each were dried in weighing glasses overnight at 105°C, the dry weight then being ascertained. The dried samples were hydrolyzed for 8 hrs. in 25-cc. measuring flasks with 4 cc. of 30 vol.% of sulfuric acid at 105°C (Heraeus drying oven). The flasks were then filled up to the mark and filtered through a dry filter.

TABLE I. CHANGES UNDERGONE BY UNTREATED WOOL YARN ON BURYING IN GARDEN SOIL*

Burial period (days)	Tensile strength (kg.)	Elongation at rupture (%)	Alkali solubility (%)	Acid solubility (%)	Cystine content (%)
(*1*) 0	2.393	32.8	12.0	14.1	11.50
(*2*) 5	2.337	30.3	12.6	14.4	—
(*3*) 6	—	—	13.1	—	—
(*4*) 10	1.869	14.5	13.5	14.9	—
(*5*) 13	1.250	7.9	13.8	—	—
(*6*) 15	not measurable		14.5	15.8	—
(*7*) 20	not measurable		15.6	17.0	—
(*8*) 25	not measurable		17.0	—	9.55

* Observations: (*4*) first appearance of mildew; (*6*) strong local attack; (*7*) considerable destruction; (*8*) agglutination and fungous threads.

One centimeter of the hydrolyzed solution was pipetted into each of three 25-cc. measuring flasks, followed by 6 cc. of acetate buffer (1,000 cc. of $2N$ sodium acetate + 300 cc. of $2N$ acetic acid). Two of the samples were then treated with 1 cc. of sulfite solution (10 g. of sodium sulfite siccum in 45 cc. of water). After 10 min. (20°C) had elapsed, all three batches were treated with 2 cc. of phosphor-9-tungstic acid reagent (Folin's reagent); they were allowed to react for 30 min. at 20°C. The solutions were made up to the mark with water. The blue solutions, together with the pale blue control solution (without sulfite), were then estimated in a 5-mm. tube in the Pulfrich photometer with an S 72 filter.

Results

The results given in Table I show the effect of the action of garden soil for 25 days on the mechanical and chemical properties of wool. It is apparent that the dry tensile strength was reduced to half its original value after 13 days, and that samples buried longer than this become so rotten that mechanical measurements were not possible.

In contradistinction to this, it is striking that the acid and alkali solubility values as well as the cystine content underwent comparatively little change. After 20–25 days decay, the samples exhibited a 40% increase in alkali solubility and a cystine content reduced by 17%. In a series of six experiments, the half-life period under the conditions described was found to lie between 14 and 16 days. It was thus possible to obtain reproducible results in the soil-burial test.

Calculation of the half-life period is illustrated in Figure 1.

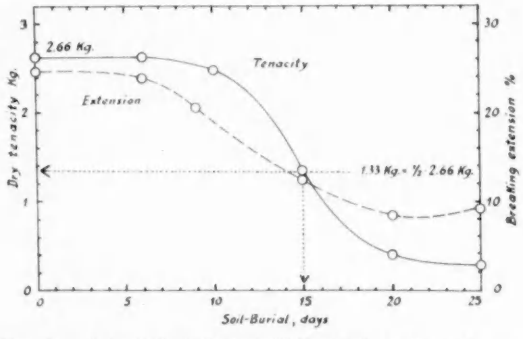

FIG. 1. *Calculation of the half-life period of wool yarns in the soil-burial test.*

TABLE II. SOME PROPERTIES OF WOOL YARN CHEMICALLY MODIFIED BY TREATMENT WITH MONOFUNCTIONAL COMPOUNDS

Chemical action	Half-life period in garden earth (days)	Alkali solubility (%)	Acid solubility (%)	Super-contraction in 50% phenol soln. (100°C, 20 min.) (%)	Cystine content (%)
Untreated	14	12.0	14.1	55.0	11.3
(*1*) Methylated with *N*/10 methanolic HCl soln.	17	15.4	17.1	5.3	—
(*2*) Reaction with epichlorohydrin (5% aqueous soln., ratio 1:30, 95°C, 2 hrs.)	>25	19.1	32.7	4.6	8.1
(*3*) Acetylation (acetic anhydride reflux, 30 min.)	>25	70.3	20.8	10.7	10.1
(*4*) Dinitrophenylation (0.8% aqueous alcoholic soln. of 2,4-dinitrofluorobenzene, ratio 1:65, 40°C, 14 hrs.)	>25	21.7	5.6	10.3	10.8
(*5*) Nitration (1% HNO_3 soln., ratio 1:75, 100°C, 3 hrs.)	10	83.3	19.9	17.4	11.7

Influence of Chemical Modification of Wool by Reaction with Monofunctional Compounds

Table II gives the results of tests on wool yarn modified by treatment with monofunctional chemical reagents. A marked increase of the resistance of wool in the burying test is observed when the wool has previously been acetylated or treated with epichlorohydrin or with dinitrofluorobenzene. These three methods of treatment were so effective that the tenacity remained unchanged after 25 days, the half-life period thus not being reached. Methylation with methanolic hydrochloric acid, however, leaves the resistance to bacterial action almost unchanged. Nitration diminishes the life of the fiber in the soil-burial test.

Figure 2 shows a graph of tensile strength plotted against time of burial.

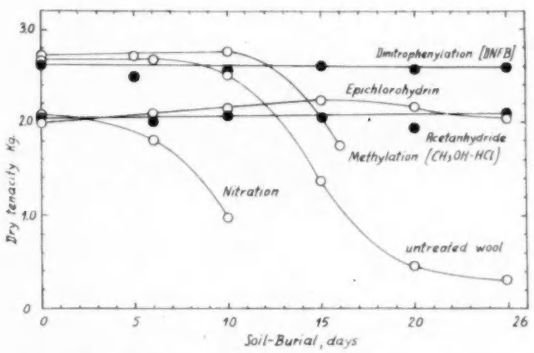

FIG. 2. *Dependence of breaking strength on the duration of the soil-burial test with chemically modified yarn samples (treated with monofunctional compounds).*

It may be seen from Table II that there is no direct relationship between acid and alkali solubility and resistance to bacterial and fungous attack, respectively. An increase of solubility in alkali was found in every case to be a result of chemical modification; the acid solubility also shows an increase, except with dinitrophenylated wool.

Chemical Modification of Wool Yarn by Reaction at the Cystine Disulfide Bond

The results of investigations are given in Table III, and the relationship between dry tensile strength and burial period is shown in Figure 3. It was to be expected that the resistance of wool to fungi and bacteria would be reduced after reductive fission of a number of the cystine bonds [*23*].

A comparison with the findings of Elöd and Zahn [*7*] on the resistance to pancreatin is interesting. It is striking that the introduction of *bis*-thioether bonds (sample (*3*)) by treatment of the reduced wool with ethylene bromide has no influence on the duration of life although the alkali solubility is strongly reduced.

Wool Chemically Modified by Treatment with Bifunctional Compounds

Table IV shows the half-life period in the soil-burial test and the chemical properties of wool after treatment with bifunctional compounds.

As illustrated in Figure 4, the samples treated with 4,6-(*bis*-chloromethyl)-1,3-dimethylbenzene, which was first used on wool by Kirst, withstood the soil-burial test best of all (half-life period = 58 days). On the other hand, formalization at pH 2, as also

TABLE III. SOME PROPERTIES OF WOOL YARN WITH CHEMICALLY MODIFIED CYSTINE

Chemical action	Half-life period in garden earth (days)	Alkali solubility (%)	Acid solubility (%)	Super-contraction in 50% phenol soln. (100°C, 20 min.) (%)	Cystine content (%)
Untreated	14	12.0	14.1	55.0	11.5
(*1*) Reduction (2.5% calcium thioglycolate soln., ratio 1:30, 50°C, 3 hrs.)	6.5	47.6	38.7	—	—
(*2*) Reduction + methylation (after reduction, with a 2.5% aqueous acetone soln. of CH_3I (0.9% with $NaHCO_3$) under reflux)	6.5	30.4	90	26.9	7.1
(*3*) Reduction + ethylene bromide (10 g. reduced wool + 5 g. dibromoethane + 2.5 g. $NaHCO_3$ in 250 cc. acetone + 50 cc. water, reflux)	6	5.4	20.2	—	7.3

TABLE IV. SOME PROPERTIES OF WOOL YARN MODIFIED BY TREATMENT WITH BIFUNCTIONAL COMPOUNDS

Chemical action	Half-life period in garden earth (days)	Alkali solubility (%)	Acid solubility (%)	Super-contraction in 50% phenol soln. (100°C, 20 min.) (%)	Cystine content (%)
Untreated	14	12.0	14.1	55.0	11.5
(*1*) Reaction with 4,6-(*bis*-chloromethyl)-1,3-dimethylbenzene (for 10 g. wool, 2.12 g. + 2.5 g. $NaHCO_3$ in 250 cc. acetone + 50 cc. water, reflux 5 hrs.)	58	6.7	16.2	8.6	6.3
(*2*) Blank test (analogous reaction without dihalogen compound)	15	7.4	—	22.3	—
(*3*) Formalization (2% CH_2O soln. in $N/20$ H_2SO_4, ratio 1:50, reflux 2 hrs.)	21	8.4	8.6	1.6	10.5
(*4*) Blank test (analogous reaction without CH_2O)	9	72.2	17.2	35.3	—
(*5*) Butandiol-*bis*-chloromethyl ether (0.3% soln. in CCl_4, ratio 1:30, 55°C, 3 hrs.)	25	6.0	9.2	—	10.0
(*6*) Blank test (0.15% soln. pyridine in CCl_4, ratio 1:30, 55°C, 3 hrs.)	17	10.7	13.4	—	11.3
(*7*) Treatment with Kaurit 140	23.5	6.7	10.9	33.2	—

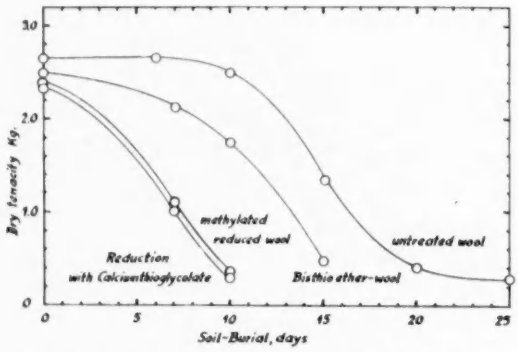

FIG. 3. *Dependence of breaking strength on the duration of the soil-burial test with chemically modified yarn samples (modification of the disulfide bonds).*

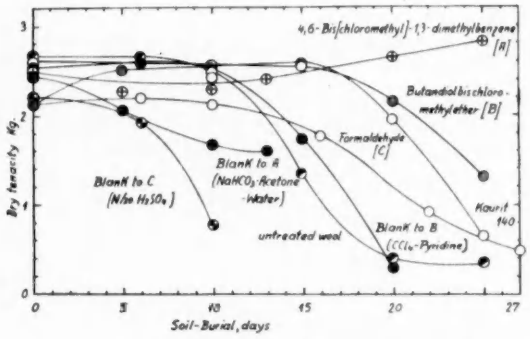

FIG. 4. *Breaking strength of yarns after soil-burial test. Chemical modification of the wool was with bifunctional compounds.*

TABLE V. SOME PROPERTIES OF CHEMICALLY MODIFIED WOOL YARN

Chemical action	Half-life period in garden earth (days)	Alkali solubility (%)	Acid solubility (%)	Super-contraction in 50% phenol soln. (100°C, 20 min.) (%)	Cystine content (%)
Untreated	14	12.0	14.1	55.0	11.5
(*1*) KCN treatment (0.1*M* KCN soln., ratio 1:50, 66°C, 16.5 hrs.)	7.5	10.5	23.4	22.4	4.0
(*2*) NaOH treatment (*N*/10 NaOH, ratio 1:50, 66°C, 16.5 hrs.)	8	4.4	16.9	12.5	5.5
(*3*) Chlorination (sodium hypochlorite soln. with 1 g. active Cl per liter, 15°C, ratio 1:30)	13	22.4	22.9	54.0	11.3
(*4*) Alcoholic potash (2% alcoholic KOH, ratio 1:100, 22°C, 15 min.)	7	13.4	17.3	—	12.7
(*5*) Heat (dry, 130°C, 24 hrs.)	14	11.8	15.9	35.8	—

TABLE VI. SOME PROPERTIES OF WOOL YARN TREATED WITH EULAN NEU AND CHLOROPHENOLS

Chemical action	Half-life period in garden earth (days)	Alkali solubility (%)	Acid solubility (%)	Super-contraction in 50% phenol soln. (100°C, 20 min.) (%)	Cystine content (%)
Untreated	14	12.0	14.1	55.0	11.5
(*1*) Eulan treatment (0.33% soln. Eulan neu in 0.13% H_2SO_4, ratio 1:30, 100°C, 1 hr.)	>25	—	—	11.1	—
(*2*) Blank test (boiled with 0.13% H_2SO_4)	23	16.5	16.8	8.9	—
(*3*) 1% alcoholic soln. 2,4,5-trichlorophenol	30	—	—	53.8	—
(*4*) 1% alcoholic soln. 2,4,5,6-tetrachlorophenol	21	—	—	50.6	—
(*5*) 1% alcoholic soln. pentachlorophenol	>32	—	—	42.9	—

treatment with the tetramethylol-acetylen-diurea compound, only sufficed to produce a moderate stabilization of the fiber against microbiological attack.

Among the chemical properties of the treated samples, the low alkali solubility is striking—*viz.*, the yarns are more resistant to alkali. The acid solubility is, however, very erratic. The large decrease in cystine content on treatment of the wool with bicarbonate in aqueous acetone is also worthy of comment (sample (*1*)).

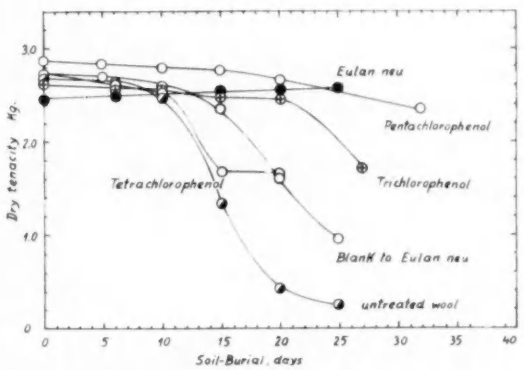

FIG. 5. *Breaking strength of some wool samples treated with some anionic aromatic compounds.*

Testing Wool Yarn Treated in a Variety of Ways

Table V presents a survey of the properties of wool treated with potassium cyanide solution, caustic soda, chlorine water, alcoholic potash, and dry heat. Each of these types of treatment causes chemical changes in the wool, as is apparent in (*1*) and (*2*) from the decrease in cystine content and in (*3*), (*4*), and (*5*) from the increase in acid solubility. The resistance of the wool samples in the soil-burial test remained unchanged in (*3*) and (*5*), whereas it was reduced approximately half in (*1*), (*2*) and (*4*). It was already known that wool submitted to oxidizing action, alkali, or boiling water is attacked more rapidly and vigorously by bacteria (Bartsch [*2*]).

Treatment with Eulan neu and Chlorophenols

The products in this group cannot be regarded as being chemically modified since the fiber has in all probability merely entered into salt formation with the anionic compound (sulfonic acid (Eulan neu), acidic chlorophenol). The chlorophenols and Eulan may thus be removed from the fiber with a suitable reagent. The Eulan molecule is bound just about as strongly as an acidic dye of moderate fastness. These products were tested so as to be able to compare their stability with that which can be achieved by chemical modification. As may be seen from Table VI and Figure 5, both wool treated with Eulan neu and that treated with pentachlorophenol were very considerably more stable in the soil-burial test than untreated wool.

It should be borne in mind here that in all cases relatively large quantities of reagent were employed. Thus, in the Eulan mothproofing treatment, approximately 3% Eulan neu is employed, whereas here we used three times this quantity.

It has already been established by Burgess [6] that wool may be rendered more resistant to bacterial attack by treatment with copper salts, chromium, Eulan N, and tannins. Mecheels and Nopitsch [18] also showed Eulanization to provide excellent protection.

Discussion

The partial substitution of the functional groups in wool proved to be very promising. Both acetylation and esterification of the carboxyl groups with epichlorohydrin considerably lengthen the life of wool. Dinitrophenylation also leads to a high degree of stabilization, but has the disadvantage of dyeing the samples yellow; it also results in poor lightfastness. Reduction of the cystine groups and methylation of the thiol groups lead to a big reduction in the resistance of wool to the fungi in the soil.

During the last 20 years, it has been stressed repeatedly that cross-linking of the polypeptide chains with bifunctional reagents must lead to stabilization of the fiber. Some of the reactions reported in the literature as those normally used for cross-linking were therefore tested for suitability in preparing a wool that is resistant to bacterial action. Surprisingly enough, the Harris process (*bis*-thioether wool) proved unsuitable. The method of wool stabilization described by Kirst was, however, well suited to the purpose. This method employs *bis*-chloromethyldimethylbenzene. The half-life period of wool protected in this manner was four times that of untreated wool.

A further series of reactions on wool was investigated in the soil-burial test. It was found that nitration, chlorination, and heat treatment do not lead to improvement of stability. The so-called "Lanthionin wool," which is prepared by treatment with potassium cyanide, is very strongly attacked and, contrary to statements in the literature, cannot be regarded as stabilized.

In so far as previous results permit judgment of the reasons for the resistance of wool to bacterial attack, it is possible to make the following statement: It is not necessary to lower the acid and alkali solubilities of the wool by chemical treatment. No direct connection was established between the alkali and acid solubilities and the half-life period.

It is unnecessary to bring about chain-linking in order to obtain a wool that is resistant to bacterial attack. It is obviously sufficient to substitute the amino and phenol groups in order to produce a resistant wool. Since, however, wool treated with bifunctional compounds simultaneously becomes more stable to alkali, this method (*e.g.*, treatment with *bis*-chloromethyldimethylbenzene) ought to be even more promising.

Previous results suggest a close analogy between cotton and wool as far as chemical modification and resistance to bacterial and fungous attack is concerned. As with cotton, acetylation of wool is a suitable method of increasing the resistance to attack by fungi. It is now assumed that acetylated and formalized cottons possess a higher degree of resistance because swelling is thereby reduced. It may therefore well be supposed that very similar considerations apply in the case of wool, especially since Bartsch [2] has already shown how bacterial resistance is enhanced by lowering the swelling capacity of the fiber with tannins.

In the meantime the present authors have proceeded with experiments to prepare a wool that is resistant to bacterial and fungous attack. An account of this work will appear in Part III of this series [28].

It was found that wool treated with 10% Eulan neu has a half-life period of 71 days, and that for yarns treated with 4,6-*bis*-chloromethyl-1,3-dimethylbenzene, the half-life can be raised to 105 days. Yarn specimens treated with dinitrofluorobenzene withstood the burial test for 115 days.

The governing factor in stabilization towards bacteria and fungi proved to be the quantity of reagent employed. A careful control and record of all experimental data (concentration of compounds, bath ratio, temperature, time of reaction) are therefore essential. A reagent should only be declared ineffective after it has been submitted to tests within a wide range of concentration.

It is at present impossible to give details concerning the application of the present results to technical practice since no experiments have as yet been carried out in this field. Also, the chemically modified yarns have not yet been submitted to other tests (abrasion-resistance, felting power, swelling, moisture adsorption, dyeing properties, etc.).

Summary

1. An attempt was made to protect wool permanently against attack by bacteria and fungi by chemical action on the functional groups.

2. Burial tests and measurements of tensile strength after periods of up to three months in garden soil served for comparison.

3. It was found that the duration of the life of wool in the soil-burial test may be raised many times by reaction with suitable bifunctional compounds. Partial substitution of amino and phenol groups also leads to a very considerable increase in resistance.

4. No direct relationship exists between the acid and alkali solubilities and the resistance to fungous attack.

Acknowledgment

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A Method of Preparing Bulk Cottons for Nep Counting*

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IT is generally agreed that some cottons are more inclined to form neps than others and that neps are made in processing [1, 4, 5]. Since neps are found in all ginned cotton, information on the number of neps in the cotton at all stages of processing is valuable.

At the present time the only quick method of counting neps is from card web. This means that the cotton has been purchased and that usually processing has begun before the first nep count is made. The time required to open bulk cotton by hand is too long for this method to be one of the tests regularly performed at the classing or receiving stage. This paper suggests a method of preparing bulk cottons for counting neps easily and rapidly. The procedure described can also be used on wastes, slivers, and rovings to find where neps are made or removed.

Procedure

Neps are most easily counted when the cotton is in a thin uniform web, as it is in card web. Such a web may be formed from bulk cottons by using the U.S.D.A. fiber blender, which feeds a sample of cotton onto the surface of a cylinder covered with card stripper clothing to produce a bat in which the fibers are distributed at random in relatively thin layers [2].

A starting sample of about 5 g. of randomly selected cotton provides enough cotton for six webs thin enough for a nep count, yet strong enough to be taken from the blender. While six counts per cotton were made during the development of this test, the results so far obtained indicate that by using this method of blending, a smaller number may be sufficient to give a representative nep count.

To form a smooth bat, the ginned cotton and other bulk cottons, such as wastes, are passed through the blender twice. Slivers and rovings, having been partially paralleled in processing, form a smooth bat with one pass. The blender is set with the feed plate 0.05 in. above the blending cylinder rather than $\frac{1}{8}$ in., as suggested by the U.S.D.A. fiber blender manual, because the narrower spacing helps form a smooth bat with less handling. It is important to reduce the amount of handling prior to counting because such handling tends to result in nep formation.

The bat is laid out lengthwise and is divided into eighths. Since the two ends are more likely to be uneven than the middle sections, they are discarded. Each of the six middle sections is then run through the blender, and a portion of each web is caught on a suitable web-counting board as the web is pulled from the blender. The neps in each sample are counted, and the samples are weighed to the nearest 0.5 mg. The number of neps per grain is then calculated:

$$\frac{\text{number of neps}}{\text{weight (g.)} \times 15.4} = \text{neps per grain.}$$

Results and Discussion

The validity of the method was checked by two tests, the first to discover if the mechanical action of the blender made neps during the test, and the second to compare counts after preparation by this method with counts on the card web for the same cottons obtained by the Clemson Fiber and Spinning Laboratory of the U.S.D.A.

To determine whether the blender makes neps, a 6-g. sample of a ginned cotton having an average number of neps was hand-blanded. One gram of this was formed into a bat which was divided by hand into six webs for counting. These were counted and weighed to give the nep count of a cotton which had had no processing other than ginning. The remaining 5 g. was treated as usual—

* A report of work done under contract with the U. S. Dept. of Agriculture and authorized by the Research and Marketing Act. The contract is being supervised by the Southern Regional Research Laboratory of the Bureau of Agricultural and Industrial Chemistry.

TABLE I. EFFECT OF MECHANICAL FIBER BLENDER ON NEP FORMATION

No. of passes	Neps/grain	Mean
0	11.9	10.9
	8.8	
	11.6	
	13.8	
	9.3	
	9.8	
2	9.7	9.9
	9.1	
	7.9	
	9.4	
	10.8	
	12.6	
10	15.4	15.6
	13.4	
	14.8	
	22.2	
	15.6	
	12.5	

TABLE II. NEP COUNTS ON SEVERAL COTTONS AT THREE PROCESSING STATIONS

Ginned cotton	Card web	Second drawing sliver
0.7	2.3	2.0
2.7	2.0	2.1
3.0	6.6	7.6
4.2	2.6	4.1
4.4	6.3	7.7
5.6	1.2	6.8
6.5	7.2	10.3
7.2	4.6	6.7
7.9	7.7	8.0
8.7	21.6	41.3
9.1	7.5	18.1
9.9	8.1	18.7
10.8	15.6	49.5
10.9	8.9	17.1
11.2	12.7	27.8
11.3	7.2	15.4
11.4	13.3	20.7
15.7	19.6	27.4
16.6	14.1	19.2
23.1	24.5	47.0
29.0	52.7	106.1

two passes through the blender followed by division into eighths. Two of these sections were made into six webs, which were counted and weighed. The remaining sample was blended eight more times (a total of ten passes through the blender), divided into eighths, and analyzed as previously described.

The results in Table I show that while the blender does make neps, it evidently does not make them at two passes, which is the number of passes used by this method for making webs.

In order to check the accuracy of the method, 21 cottons were counted at two stations—ginned cotton and second drawing sliver. The values obtained were compared with counts taken for the same cotton samples at the card web stage by the Clemson Fiber and Spinning Laboratory, U.S.D.A. [3]. Table II gives the nep counts for each cotton at each of the three stations. The ginned cotton shows slightly lower values than card web, the second drawing sliver consistently higher ones.

Neps were counted at nine processing stations for two cottons on which methods, rates, and conditions of processing were carefully controlled. Six counts were made for each processing station. The cottons were a matched pair of rain-grown and irrigated cottons used as master samples in processing studies.

These two cottons are very much alike in maturity (84% and 87%), fineness (4.1 and 4.2 μg./in.), and in other conventional fiber properties, and were processed under as nearly identical conditions as possible. The results in Table III indicate clearly that processing more than doubles the number of neps present in the cotton. The processes making the most neps were carding and roving. Combing removes many neps, but drawing and roving again increase the number.

TABLE III. EFFECT OF PROCESSING ON NEP FORMATION

Processing station		Neps/grain Cotton *A*	Neps/grain Cotton *B*
Ginned cotton		9.1	10.5
Opened cotton		11.4	11.2
Picker lap		12.2	12.1
Card sliver		19.1	19.9
Second drawing sliver		20.2	20.6
Roving		25.5	25.0
Comber sliver	with 16% noils removed	5.5	4.5
Finished combed sliver	with 16% noils removed	6.9	6.4
Combed roving	with 16% noils removed	9.4	7.0

Summary

It has been shown that the nep count of a cotton sample can be determined quickly and easily when ginned cotton, sliver, roving, or waste is prepared for counting with the aid of a mechanical blender of the type developed by the U. S. Dept. of Agriculture. The time required for six counts on one sample is about 30 min., which is considerably less

than that needed if preparation is by hand. The method permits a rapid evaluation of nep content at all stages in cotton processing prior to yarn spinning.

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Modification of Wool by the Application of Linear Synthetic Polyamides

Part III: Pretreatment of Wool*

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Abstract

The presence of foreign materials such as soaps and oils on wool interferes with the deposition of *N*-alkoxymethyl polyamides when used for the prevention of felting shrinkage.

If the wool is rigorously cleaned by ethanol extraction or if the fiber surface is modified by pretreatment with hydrogen peroxide or other reagent, then the resin is able to attain its maximum effect and approximately 3% resin (based on the weight of the wool) is sufficient to prevent felting shrinkage.

It is suggested that both forms of pretreatment tend to improve adhesion between resin and fiber and so render the resin deposit more effective in preventing felting.

Introduction

It has been shown [7, 8] that modified nylon resins containing alkoxymethyl and/or hydroxymethyl groups can be used to prevent felting shrinkage of wool fabrics. The fabric used in the above work was successively Soxhlet-extracted with petroleum ether and 95% ethanol before treatment.

When this process was used on a pilot-plant scale, it soon became apparent that the alcohol extraction was an essential part of the process. If it was omitted, then much greater amounts of resin were required to give satisfactory reduction in felting shrinkage. The effect of possible contaminants such as soaps and oils on the felting shrinkage of resin-treated fabric was therefore investigated, and the effect of modifying the fiber surface without removing contaminants, by pretreatment with hydrogen peroxide, has also been examined.

Materials and Methods

N-Methoxymethyl Nylon

Type CA nylon (DV-42) containing 8.2% total formaldehyde was obtained from Imperial Chemical Industries Ltd., Blackley, England.

* Parts I and II appeared in the March, 1951, and September, 1951, issues, respectively.

Wool

Two commercially scoured worsted fabrics (*A* and *B*) were used. Supplies of *A* were exhausted before the work was completed, and it was necessary to continue with *B*, which had a slightly different construction. Fabric constructions were as follows:

	A	*B*
Weave	plain	plain
Warp yarn	2/30's worsted	2/30's worsted
Weft yarn	2/30's worsted	2/30's worsted
Ends/in.	35	27
Picks/in.	27	20
Weight (oz./sq. yd.)	5.0	3.4

Felting Shrinkage

All tests were carried out in a washing machine of the horizontal cylindrical rotating cage type, using 0.05% soap solution at 37°–40°C. Up to forty 6 in. square samples were washed in one run, and area shrinkage was measured as described previously [7, 8]. The washing of treated samples was continued until untreated controls had shrunk 40% in area. This time varied, being about 30 min. for fabric *A* and 12 min. for fabric *B*.

Experimental Procedure and Results

Soxhlet Extraction of Fabric

Samples of fabric *A* were treated in solutions of varying concentration of methoxymethyl nylon resin in 75% aqueous ethanol (75 ethanol/25 water, v/v) and hydrolyzed in 2*N* HCl at 25°C for 30 min., according to the procedure described previously [8].

Similar fabric samples were Soxhlet-extracted for 6 hrs. (*ca.* 25 siphonings) with 95% ethanol and then treated as above. All samples were conditioned at 65% R.H. and 70°F, and were weighed before and after treatment in order to determine the amount of resin deposited.

The effect of ethanol extraction on the felting shrinkage of these treated fabrics is shown in Table I.

It was found necessary to pretreat the fabric in order to obtain effective results with small amounts of resin.

The greater effectiveness of the resin when applied to solvent-extracted fabric may be attributed to: (*a*) removal of contaminants such as soaps and oils or (*b*) physical or chemical modification of the fiber surface during extraction.

Effect of Contaminants on Resin Efficiency

The following were chosen as representative of most classes of contaminants likely to occur on scoured wool: stearic acid soap, oleic acid soap, anionic, cationic, and nonionic detergents, oleic acid, mineral oil, Oliva 431, and wool wax.

Sodium *secondary*-alkyl sulfate, isolated from Teepol 610 (Shell), was used as the anionic, cetyl pyridinium chloride as the cationic, and Lubrol W (I.C.I.) as the nonionic detergent. Oliva 431 (Shell) is a mineral oil containing additives to assist emulsification in scouring.

These materials were applied to wool fabric *A* which had previously been Soxhlet-extracted for 6 hrs. with 95% ethanol. The fabric was immersed in a solution of the contaminant, squeezed in a wringer, dried, and then rinsed in several changes of water. Aqueous solutions were used for the soaps and detergents, and the other materials were dissolved in suitable organic solvents. The fabrics were then given a normal resin treatment, using resin solutions of varying concentration to give a range of resin contents on the wool.

Results of the washing tests are given in Table II.

Mineral oil has the least effect on felting shrinkage, and the anionic detergent has less effect than other contaminants.

Even if the wool is almost free from contaminants, however, it is possible that they could accumulate in the resin solution if one solution were used for a number of treatments, as could be the case under industrial conditions. The effect of contaminants when added to the resin solution was therefore examined. Results are given in Table III for fabric *B*.

TABLE I. EFFECT OF SOXHLET EXTRACTION ON THE FELTING SHRINKAGE OF FABRICS SUBSEQUENTLY RESIN-TREATED

Not extracted		Extracted	
Resin (%)	Area shrinkage (%)	Resin (%)	Area shrinkage (%)
7.8	14	8.8	0
5.1	24	6.3	0
3.2	32	4.2	0
2.1	34	3.1	0
1.2	35	2.1	3
0	38	0	38

TABLE II. EFFECT OF CONTAMINANTS ON THE FELTING SHRINKAGE OF RESIN-TREATED FABRICS

Contaminant	Amount on wool (%)	Resin (%)	Area shrinkage (%)
Crest chips*	1.0	5.9	25
(stearic acid soap)	1.0	3.4	37
	1.0	2.4	41
Cyco soap*	1.0	5.5	34
(oleic acid soap)	1.0	3.1	42
	1.0	2.0	43
Sodium *sec*-alkyl sulfate	0.9	6.5	0
	0.9	3.0	6
	0.9	1.9	9
	0.9	1.5	35
Cetyl pyridinium chloride	0.9	5.7	39
	0.9	1.0	47
	0.9	0.6	38
Lubrol W	0.7	5.8	35
	0.7	1.5	40
	0.7	0.7	40
Oleic acid	1.1	6.2	13
	1.1	3.7	32
	1.1	2.7	37
Mineral oil	1.2	6.1	0
	1.2	2.9	0
	1.2	1.2	21
Oliva 431	2.2	6.0	13
	2.2	3.9	24
	2.2	2.8	31
Wool wax	2.4	5.8	16
	2.4	3.8	23
	2.4	2.4	33
None	0	6.8	0
	0	3.2	0
	0	2.2	2
	0	0	41

* Obtainable from J. Kitchen & Sons Pty. Ltd.

TABLE III. EFFECT OF ADDING CONTAMINANTS TO THE RESIN SOLUTION ON THE FELTING SHRINKAGE OF TREATED FABRICS

Contaminant	Solution composition: Contaminant (%)	Resin (%)	X*	Y†	Area shrinkage (%)
Crest chips	0.1	3	5.1	0.8	32
	0.5	3	3.7	1.5	38
	1.0	3	3.5	1.4	39
	0.1	6	8.5	0.5	7
	0.5	6	8.7	1.0	11
	1.0	6	8.8	0.7	13
Cyco soap	0.1	3	4.4	1.6	37
	0.5	3	3.0	1.3	38
	1.0	3	2.9	1.3	39
	0.1	6	8.8	0.4	13
	0.5	6	9.0	0.5	12
	1.0	6	8.4	0.3	14
Sodium *sec*-alkyl sulfate	0.1	3	5.0	0.3	32
	0.5	3	4.6	0.6	25
	1.0	3	4.9	0.6	27
	0.1	6	7.3	0.4	6
	0.5	6	7.2	0.2	2
	1.0	6	7.6	0.5	6
Cetyl pyridinium chloride	0.1	3	5.5	0.9	34
	0.5	3	4.3	1.6	38
	1.0	3	4.0	1.8	39
	0.1	6	7.8	0.7	18
	0.5	6	8.1	0.3	18
	1.0	6	8.2	0.5	18
Lubrol W	0.1	3	4.4	1.1	35
	0.5	3	3.0	0.7	36
	1.0	3	3.3	1.0	37
	0.1	6	7.5	0.1	21
	0.5	6	7.7	0.5	22
	1.0	6	7.8	0.4	22

* X = % increase in weight after resin treatment (resin and contaminant).

† Y = % loss in weight after additional extraction with ethanol (contaminant).

Mineral oil and Oliva 431 are not very soluble in the resin solution, but they were taken up by the fabric, as indicated by the X values. The results are similar to those given in Table II—*i.e.*, mineral oil has the least effect, and the anionic detergent has less effect than other contaminants.

The contaminants show the following approximate decreasing order of interference with resin deposition: cationic detergent, nonionic detergent, oleic soap, stearic soap, Oliva 431, wool wax, anionic detergent, mineral oil.

The presence of soaps, detergents, and oils either in the resin solution or on the fiber can thus reduce the effectiveness of the resin deposit. But it does not necessarily follow that if the wool is cleaned of all contaminating matter the resin will attain its maximum effect. It is possible that ethanol extraction not only removes such compounds but also modifies the fiber surface. It has been reported that hot alcohol can remove protein matter from wool [9], and Haller stated that it can modify the surface to such an extent that the scales become pitted [6].

TABLE III.—*Continued*

Solution composition					
Contaminant	Contaminant (%)	Resin (%)	X*	Y†	Area shrinkage (%)
Oleic acid	0.1	3	5.1	0.4	31
	0.5	3	5.8	0.8	24
	1.0	3	6.4	1.5	20
	0.1	6	8.2	1.1	12
	0.5	6	8.7	1.2	9
	1.0	6	9.7	1.7	10
Mineral oil	0.1	3	7.7	2.5	2
	0.5	3	11.4	7.1	2
	1.0	3	17.6	13.9	9
	0.1	6	9.9	1.5	1
	0.5	6	14.0	6.0	0
	1.0	6	8.4	11.2	1
Oliva 431	0.1	3	7.4	1.9	35
	0.5	3	11.0	7.9	35
	1.0	3	16.3	14.1	41
	0.1	6	9.4	2.4	18
	0.5	6	15.3	8.4	18
	1.0	6	20.4	14.5	22
Wool wax	0.1	3	4.7	0.1	0
	0.5	3	3.0	0.9	18
	1.0	3	2.9	0.7	17
	0.1	6	6.4	0	0
	0.5	6	7.0	1.0	5
	1.0	6	9.0	3.4	12
	Fabric not extracted				43

Cold ethanol would be much less likely to modify the fiber surface than the hot solvent, and so further Soxhlet extractions were carried out for varying times, both with hot and cold 95% ethanol, and the amount of extract and area shrinkage of the resin-treated fabrics were determined (Table IV).

"Hot" extractions were carried out in a conventional Soxhlet extraction apparatus with reflux condenser. "Cold" extractions were also carried out in a Soxhlet apparatus, but the distillate from the reflux condenser was passed through an extra condenser before entering the extractor.

Although a short extraction with hot ethanol is an effective pretreatment, a considerably longer extraction is necessary with cold ethanol. Further, the amount of material extracted is not a reliable guide to the efficiency of the pretreatment. These results suggest that little or no fiber-surface modification is necessary if the wool is left in a sufficiently clean condition, as cold ethanol would not be expected to modify the fiber surface significantly. With hot ethanol, where slight fiber-surface modification may occur,

TABLE IV. EFFECT OF SUCCESSIVE ETHANOL EXTRACTIONS ON RESIN TREATMENT

Soxhlet extraction	No. of siphonings	Extract (%)	Resin (%)	Area shrinkage (%)
"Hot" 95% ethanol	1	1.10	2.9	1
	2	1.20	3.0	0
	5	1.27	3.5	0
	10	1.30	2.8	0
	20	1.45	2.6	0
	30	1.48	2.5	0
	40	1.50	2.9	0
"Cold" 95% ethanol	25	1.06	4.9	24
	50	1.41	4.4	2
	80	1.50	4.2	2
None			3.3	31
			0	40

the pretreatment becomes effective before all of the contaminating material has been removed.

Hydrogen Peroxide Pretreatment

Hydrogen peroxide has been used for the treatment of wool prior to the application of methylol melamine resins [1], and Fluck stated [5] that the pretreatment causes the tips of the scales to be loosened from the fiber, which may increase adsorption and anchorage of the resin at these points. The effect of hydrogen peroxide pretreatment as an alternative to alcohol extraction was therefore investigated.

Preliminary experiments showed that sodium pyrophosphate stabilizer gave more satisfactory results than sodium metasilicate, and so the former was used in all experiments.

Samples of both fabrics *A* and *B* were pretreated for varying times with varying strengths of hydrogen peroxide solution containing 0.8% sodium pyrophosphate at pH 10 and 50°C. The liquor : wool ratio was 20 : 1. The samples were washed until neutral and then given a normal resin treatment.

The effects on felting shrinkage of hydrogen peroxide alone and of hydrogen peroxide followed by resin treatment are given in Figures 1 and 2 and Table V.

These results indicate that different fabrics may require widely differing conditions of peroxide pretreatment before the resin becomes effective. In interpreting results, care should be taken to ensure that any reduction in felting obtained is not the result of the bleaching operation, which can also cause reduction. In order to prevent undue weakening of

TABLE V. EFFECT OF HYDROGEN PEROXIDE PRETREATMENT ON THE FELTING SHRINKAGE OF RESIN-TREATED FABRICS

H_2O_2 concentration (vols.)	Time (min.)	Fabric *A* Resin (%)	Fabric *A* Area shrinkage (%)	Fabric *B* Resin (%)	Fabric *B* Area shrinkage (%)
1	0	2.4	36	8.1	33
	30	3.3	1	5.8	21
	60	3.8	1	6.8	17
	80	3.6	0	6.7	20
	120	3.7	0	6.7	6
	150	3.6	0	6.2	17
	180			6.2	9
	240			5.6	6
2	0	2.4	36	6.8	23
	20	3.0	0	6.1	19
	40	3.4	0	7.4	10
	60	3.7	0	6.7	6
	80	3.7	0	6.4	5
	100			5.9	1
	120			5.5	2
	180			5.8	1
4	0	2.4	36	3.9	25
	10	3.1	1	3.9	17
	20	3.2	0	3.6	15
	30	3.2	0	4.0	13
	40	3.4	0	4.4	4
	50			4.3	2
	60			4.0	1
	90			3.6	0
No pretreatment		0	39	0	42

the wool, it is advisable to use the least drastic conditions of pretreatment consistent with an effective resin treatment.

Treatment with Methylol Melamine Resin

The hydrogen peroxide pretreatment has already been described [5] in connection with resin processes using methylol melamine resins for prevention of felting shrinkage of wool. In order to determine whether extraction with ethanol is equally effective with these resins, samples of fabric *A* were: (*a*) pretreated with 2 vols. H_2O_2 for 1 hr. at 50°C in a bath containing 0.8% sodium pyrophosphate at pH 10, (*b*) extracted with 95% ethanol in a Soxhlet extractor, and (*c*) given no pretreatment.

They were then treated with a Lanaset type resin [4] known as Beetle Resin M310 according to the method described by Beetle-Elliott Ltd. [2].

Felting shrinkage results are given in Table VI.

As with alkoxymethyl polyamides, it is necessary to apply a pretreatment to the fabric if the maximum effect is to be obtained from the melamine resins, and both ethanol extraction and immersion in hydrogen peroxide solution are suitable pretreatments.

Discussion

If the felting of wool is to be prevented by the use of the least possible amount of resin, it is apparent

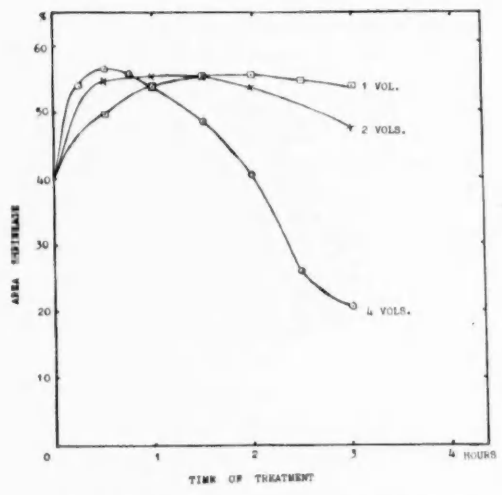

FIG. 1. *Effect of hydrogen peroxide pretreatment (0.8% $Na_2P_2O_7$, pH 10, 50°C) on felting shrinkage of fabric A.*

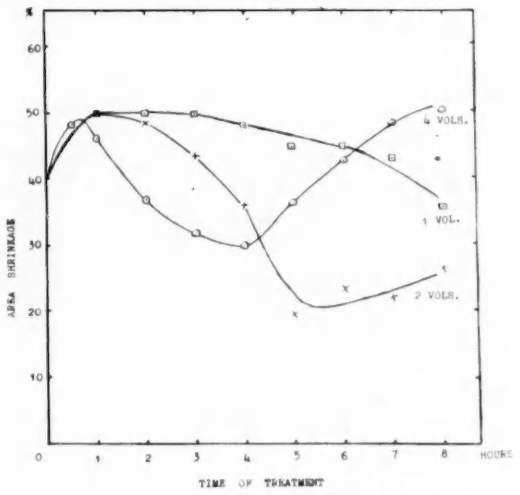

FIG. 2. *Effect of hydrogen peroxide pretreatment (0.8% $Na_2P_2O_7$, pH 10, 50°C) on felting shrinkage of fabric B.*

TABLE VI. FELTING SHRINKAGE OF WOOL FABRIC TREATED WITH METHYLOL MELAMINE RESIN

Pretreatment	Resin (%)	Area shrinkage (%)
2 vols. H_2O_2	4.7	0
2 vols. H_2O_2	6.2	0
95% ethanol extraction	6.4	4
95% ethanol extraction	6.7	1
None	3.7	42
None	8.6	24
None	0	42

from the experimental evidence described above that a pretreatment is necessary in addition to normal finishing treatments. Suitable pretreatments include extraction with hot ethanol, hydrogen peroxide bleaching, and probably other treatments which either clean the wool or modify the surface structure of the fiber.

The Melafix process of Ciba Ltd. is probably a combination of chlorination and resin treatments, while a combination of alcoholic alkali and melamine resin processes has also been used to prevent the felting shrinkage of wool [3]. In both of these "combined" processes, the chemical modification may be considered as a pretreatment for the resin application. Although many of these pretreatments can adequately reduce the felting shrinkage of wool per se if carried far enough, it is not necessary to take them to this stage for them to be effective pretreatments for the resin process. This will be seen from Table V, where immersion of fabric *A* in 1 vol. hydrogen peroxide at 50°C for 30 min. does not reduce the felting shrinkage by itself, yet is a satisfactory pretreatment for the resin treatment.

Although soaps, oils, and other materials can reduce the efficiency of the resin, whether they be on the wool or in the resin solution, it seems certain that the function of the hot alcohol extraction as a pretreatment is twofold: (*a*) it removes extractable matter from the wool and (*b*) it modifies the fiber surface. Surface modification is not sufficiently severe to be detected under the microscope. Figure 3 shows typical casts of fibers which have been (*a*) treated with hydrogen peroxide solution, (*b*) extracted with hot ethanol, and (*c*) untreated. Only the peroxide-treated fibers show signs of scale damage. When samples of fabric extracted with hot ethanol and cold ethanol, respectively, were dyed in the same bath with the unextracted fabric, using Naphthalene Scarlet 4RS, the fabric extracted with the hot solvent dyed to a deeper shade than the others. This suggests that slight surface modification results from the hot extraction. The combination of complete removal of extraneous matter and slight surface modification brought about by extraction with hot ethanol suffices to give an effective pretreatment. Prolonged extraction with cold ethanol, which causes no surface modification but completely removes extraneous matter, is also effective. On the other hand, hydrogen peroxide treatment, which does not remove all extraneous matter but causes considerable surface modification, is equally effective. It would appear, then, that with extremely clean wool only slight surface modification is necessary, whereas with moderately

FIG. 3. *Fiber-cast photographs:* (a) *after treatment for 2 hrs. with 2 vols.* H_2O_2 *containing 0.8%* $Na_4P_2O_7$ *at pH 10 and 50°C,* (b) *after Soxhlet extraction with 95% ethanol for 6 hrs., and* (c) *untreated fiber.*

clean or even dirty wool a more severe surface modification is required before the maximum effect is obtained by the resin deposit.

It is possible to reduce considerably the felting shrinkage of a fabric which has not been pretreated by applying a larger quantity of resin. While the use of large amounts of resin is generally not favored on the grounds of economy and harshness of handle, it is of interest to note that for a given amount of resin the alcohol-extracted fabric has a much harsher handle than a fabric which has received no pretreatment. For example, an alcohol-extracted fabric containing about 3% resin has a similar handle to an unextracted fabric with about 6% resin. In general, it was found that the harsher the handle after a given resin treatment, the more effective was the resin deposit in preventing felting, particularly in repeated washing.

The two forms of pretreatment—*viz.*, fiber cleansing and fiber-surface modification—are thought to be effective because both will tend to increase adhesion between fiber and resin and so result in greater reduction in felting. Oils and soaps which are able to spread over the fiber surface will form a barrier between resin and fiber, with consequent reduction in adhesion between them. Hence, a resin deposit on an untreated fabric will not withstand repeated washing because of the presence of residual soap and possibly oils from the final scouring operation. Mineral oil, which has no polar groups, would be less likely to form such a barrier, and so causes less interference than soaps.

It is unlikely that a pretreatment which only cleaned and did not modify the fiber surface—*e.g.*, cold ethanol extraction—would be industrially practicable: an optimum pretreatment would be one which combined both cleaning and surface modification of the fibers. As reagents which modify the surface often tend to cause fiber weakening, a pretreatment which brought about appreciable cleaning and only slight fiber modification would be preferred to one which gave poor cleaning but appreciable surface modification.

These remarks apply to the treatment of wool with alkoxymethyl nylon resins; it is likely that they are equally applicable to other types of resin.

Conclusions

1. In order that alkoxymethyl polyamide resins may achieve their maximum effect in preventing the felting shrinkage of wool, it is necessary that the fabric receive a pretreatment, such as extraction with hot ethanol or treatment with alkaline hydrogen peroxide solution.

2. The function of the pretreatment is either to cleanse the wool from impurities such as soaps and oils, which interfere with the subsequent resin deposition, or to modify the fiber surface, or it may be a combination of these actions, both of which will improve fiber-resin adhesion.

It seems likely that the more efficient the cleaning operation, the less severe the surface modification needed in order to achieve the same effect with a given amount of resin.

Acknowledgments

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Measurement of Friction Between Single Fibers

Part VII: Physicochemical Views of Interfiber Friction*

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DURING the last few years, interest in the frictional properties of textile materials has increased steadily. The importance of frictional properties in textile processes, such as carding, drawing, spinning, and fulling, is recognized, and their importance for the properties of finished products, such as breaking strength and elastic properties of yarns and fabrics, handle, creasing, and abrasion of fabrics, has been pointed out.

At the Swedish Institute for Textile Research, we have concentrated on the interfiber friction—*i.e.*, the friction between single individual fibers. There are well-known analogies (and also differences) between the structure of fibers and the structure of yarns, where the fibers may be called the "molecules" of the yarn. The cohesional forces between the molecules in a fiber correspond at least partly to the frictional forces between the fibers in a yarn. Therefore, for knowledge of the textile behavior of fibers a thorough knowledge of the interfiber friction is essential. The authors have studied it for several years, and have reported previous work in TEXTILE RESEARCH JOURNAL [3, 5, 6, 7, 8, 9].

There are two classical laws of friction which have been ascribed to the French scientist Amontons, who stated them in 1699, but they were known earlier by Leonardo da Vinci and were mentioned in his *Notebooks*. These laws tell us (*1*) that the force of friction is independent of the contact area of bodies which are sliding on one another, and (*2*) that the force is proportional to the load acting perpendicularly to these surfaces—*e.g.*, the ratio between frictional force and load is constant. This ratio is called the "coefficient of friction," and is denoted by μ.

Amontons' laws are only approximately valid. They hold fairly well for metals, ice, and other hard materials, but are less valid for fibers and other relatively soft materials. The coefficient of friction is not constant for fibers, but decreases when the load increases. This is shown by Figure 1, which gives the relation between frictional force, F, and load, W, for two viscose fibers. These measurements were made on the point friction meter, where two fibers cross each other at a small angle and the friction is measured at the point of contact [3]. The curve for static friction, which is the force necessary for starting the movement, follows an almost straight line, which indicates a constant μ. There is a slight curvature of the line, but there is a more pronounced curvature for the kinetic friction.

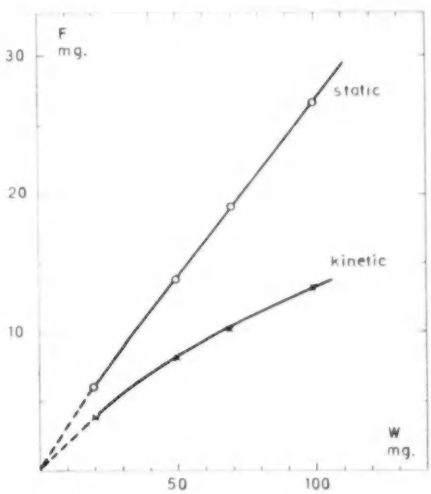

FIG. 1. *Static and kinetic friction between two viscose fibers.* F = *frictional force,* W = *load. Measurements were made on the point friction meter.*

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which is the force necessary to keep the fibers moving. When using the formula

$$\mu = \frac{F}{W}, \tag{1}$$

we find a decreasing μ with increasing W. As a first approximation a linear relationship is empirically found between μ and $1/W$ (Figure 2). A similar picture is found for other fibers—*e.g.*, wool (see figures in [5]).

What is the cause of friction, and how can Amontons' laws and the deviation from them be explained? The first question that arises in the studies of these phenomena is this: how great is the real area of contact? It is obvious that rough surfaces, such as emery cloth and unpolished wood, can never come into intimate contact. But it has been shown that not even the most polished surfaces are plain if they are seen from a molecular point of view [1]. The best polishing can decrease the asperities to a height of 1000 Å. or even 100 Å., but even such a well-polished surface shows peaks and valleys with level differences of hundreds of atoms. Even the best smooth reflecting surface of glass or metal has peaks of the height of thousands of atoms. When two bodies with such surfaces are placed one upon another, the real contact area is therefore much smaller than the apparent contact area and is limited to just a few points, but these points carry an enormous pressure.

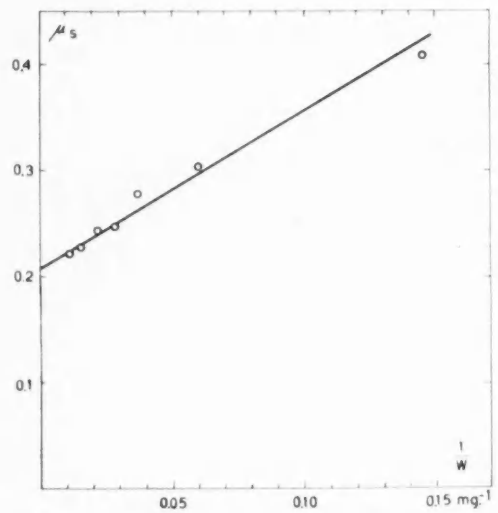

FIG. 2. *Relation between static coefficient of friction, μ_s, and 1/W for viscose fibers. Measurements were made on the point friction meter.*

Bowden and Tabor [1] in their book on friction reviewed methods for measuring asperities and contact areas on polished surfaces. For steel surfaces it was found that the real area of contact is often less than .0001 of the apparent area of contact. The most interesting result, however, is that the real area of contact is independent of the apparent area of contact. The pressure on the small contacts will depress the apices like clay, until the areas are large enough to carry the load without further deformation. This compression gives rise to an adhesion or even welding between the surfaces, and the explanation of friction follows that shearing forces are necessary to break the welds.

Bowden and Tabor advanced the theory that for all types and shapes of surface irregularities the real area of contact is almost proportional to the load if the deformation is considered to be plastic. This can be expressed

$$A = \frac{W}{p_m}, \tag{2}$$

where A is the real area of contact and p_m is the yield pressure of the asperities. The frictional force is the shearing force required to break the welds, and therefore is proportional to the area of the welds, A. We can therefore write

$$F = As, \tag{3}$$

where s is the force per unit area which is necessary to shear the junctions. Combining equations (2) and (3) gives

$$\frac{F}{W} = \frac{As}{Ap_m} = \frac{s}{p_m} = \text{constant}, \tag{4}$$

and this is Amontons' second law, with $\mu = s/p_m$. This discussion also explains the first law—that the friction is independent of the apparent area of contact.

This theory holds for metals and other hard materials with a high modulus of elasticity. The deformations are not extended over large areas, but are localized around the contact asperities; therefore, the deformations are almost exclusively plastic. With soft materials the situation is somewhat different. The deformations cover larger areas and therefore the local pressure is smaller, which means that the pressure might not exceed the yield point

of the material for a large portion of the contact area, even if the yield point (or yield region of the pressure-deformation curve) is considerably lower than for metals. Therefore, part of the deformation may be elastic and may be recovered if the pressure is released.

The elastic deformation does not give formulas which are as simple as those for the plastic deformation. We have treated the problem for the twist friction meter, which has been used very extensively for our measurements [5]. In that apparatus two fibers of equal or almost equal thickness are twisted a few turns at a small angle of twist (Figure 3). The fibers can be treated approximately as two cylinders with a contact line along a mutual generatrix. The small twist only keeps the cylinders from sliding apart in a transverse direction.

The area of contact falls along a straight (or almost straight) line, the mutual generatrix. Since the material is rather soft and bendable, it may be assumed that the contact is real along a considerable part of the contact line.

Hertz [4] calculated the distribution of pressure and the width of the deformation area for elastic bodies of various shapes and also for two parallel cylinders. His formulas are valid for small elastic deformations.

FIG. 3. *Fiber twist in the twist friction meter.*

They show that the pressure is distributed elliptically across the deformation area (Figure 4). The maximum pressure (at the central line of the contact area) is

$$p_{\max} = \frac{2W}{\pi r l}, \tag{5}$$

where r is half the width of the contact area and l is the length of the area or the cylinders. The width of the area is obtained from the formula

$$r^2 = \frac{4WR \times 0.91}{\pi E l}, \tag{6}$$

where R is the radius of each of the cylinders and E is the modulus of elasticity of the material. Combining equations (5) and (6) gives

$$p^2_{\max} = \frac{WE}{\pi l R \times 0.91}. \tag{7}$$

If the radii of the cylinders are different, R_1 and R_2, R in the above formulas is substituted by the harmonic means of the radii

$$\frac{2}{R} = \frac{1}{R_1} + \frac{1}{R_2}.$$

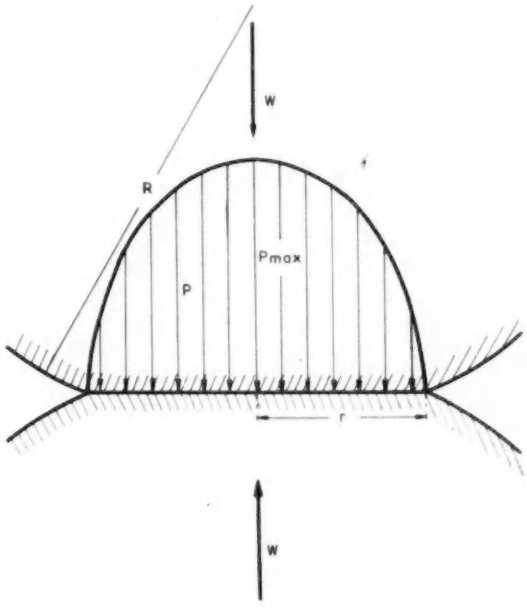

FIG. 4. *Distribution of pressure during elastic deformation between two cylinders with radius* R.

If the limit of elasticity is exceeded, a plastic flow will first occur around the middle of the contact area, but two zones with elastic deformation will be left at the outer limits of the area of contact. For the sake of simplicity it is supposed that the limit of flow is well defined. In general, with plastic materials this is not true because the elastic and plastic deformations overlap considerably, but this will probably not essentially influence the result of the following calculation. If this approximation is made, the general picture of the pressure distribution will be as shown in Figure 5, with a constant maximum pressure, p_m, in the middle zone and symmetrically decreasing pressure in the two side zones with supposedly purely elastic deformation. The shape of the pressure distribution curve in these zones must be discussed further. In Figure 5 are given three conceivable alternatives: *I*, *II*, and *III*. For *I* the pressure is distributed ellipsoidically, and the axes of the ellipsoid are the maximum pressure, p_m, and the width of the elastic zone, $r_t - r_p$, where r_t is half the total width of the deformation and r_p is half the total width of that part of the deformation which is partly plastic. This case is conceivable because the pressure distribution curve probably should not have a point of discontinuity at $r = r_p$.

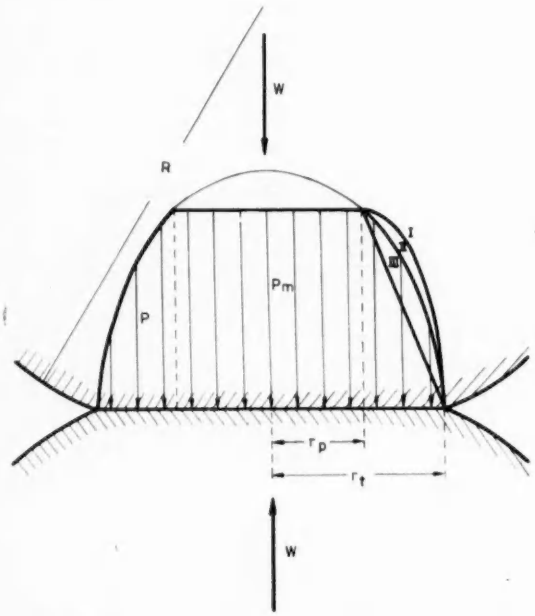

FIG. 5. *Distribution of pressure between two cylinders when the deformation is partly plastic and partly elastic.*

For the second conceivable case, *II*, it is supposed that the pressure in the elastic zone is the same as if no plastic deformation had occurred—*i.e.*, the curve has the same shape as in Figure 4. A lower limit, *III*, is given simply by a straight line. Cases *I* and *III* represent the extremes.

The total load, W, is given by the equation

$$W = \int p dA = 2 \int_0^{r_t} p l dr, \tag{8}$$

where A is the area of contact, l is the length of A, and p varies with r according to the picture given in Figure 5. A simple geometrical calculation gives

$$W = 2p_m l r_p + l p_m (r_t - r_p) \frac{\pi}{2} \tag{9}$$

for case *I*.

For an approximate estimation of the width of the elastically deformed area, $r_t - r_p$, we may use formulas (5) and (6), putting $p_{max} = p_m$,

$$r = r_t - r_p,$$

which gives

$$r_t - r_p = \frac{2p_m R \times 0.91}{E}. \tag{10}$$

From equations (9) and (10) we obtain

$$r_t = \frac{W}{2lp_m} + \frac{2p_m R \times 0.91}{E} \left(1 - \frac{\pi}{4}\right). \tag{11}$$

The total area of contact is

$$A = 2lr_t, \tag{12}$$

and by the application of the theory given in equation (3) we obtain

$$F = \frac{sW}{p_m} + \frac{asl R p_m}{E}, \tag{13}$$

where a is a constant $= 4 \times 0.91 \ (1 - \pi/4) = 0.78$.

It is easy to see that for case *III* the factor $(1 - \pi/4)$ will be replaced by a factor $1/\pi$, which gives $a = 1.16$.

Therefore, we may assume a general equation of the form

$$F = \alpha W + \beta l R, \tag{14}$$

where α and β are constants with the following relations:

$$\alpha = \frac{s}{p_m} \quad \text{and} \quad \beta = \frac{as p_m}{E}. \tag{15}$$

TABLE I

Nylon fiber No.	α	β	Rest term, Δ
1	0.263	4.55×10^2	0.21
2	0.250	3.33×10^2	0.07
3	0.236	2.65×10^2	0.07
4	0.277	4.24×10^2	0.03
average	0.257	3.67×10^2	0.10

TABLE II

Nylon fiber No.	Partial coefficients of correlation $r_{FW \cdot l}$	$r_{Fl \cdot W}$
1	0.9898	0.7797
2	0.9933	0.6378
3	0.9911	0.6077
4	0.9966	0.8694

For case *II* the calculations become more tedious. It has been found, also under the same assumption, that an equation of the same form as equation (14) gives a good approximation of the results, but then

$$\alpha = s \cdot f_1(p_m)$$

and

$$\beta = \frac{4 \times 0.91 \times s}{E} \cdot f_2(p_m), \tag{15a}$$

where f_1 and f_2 are implicit functions of p_m and can be evaluated graphically.

If the deformation is purely elastic, p_m should be calculated from Hertz's formula; we obtain

$$F = \gamma \sqrt{WlR}, \tag{16}$$

where

$$\gamma = \frac{s}{\sqrt{E}} \times 4\sqrt{\frac{0.91}{\pi}} = \frac{2.15 \times s}{\sqrt{E}}. \tag{17}$$

It is therefore obvious that from theoretical aspects we obtain deviations from Amontons' laws both for the purely elastic and for the semielastic-semiplastic deformations. These laws will hold only for completely plastic deformations.

Dividing equations (14) and (16) by W gives

$$\mu = \frac{F}{W} = \alpha + \beta \frac{lR}{W} \tag{14a}$$

and

$$\mu = \frac{F}{W} = \gamma \sqrt{\frac{lR}{W}}. \tag{16a}$$

As shown before, an approximately linear relation between μ and $1/W$ is found experimentally for fibers (see Figure 2).

Experiments with nylon and polyester fibers (Terylene) show that the relation (14) holds well for these fibers also. They are uniform in thickness and have a circular cross section, and are therefore suitable for such experiments. The measurements were made on the twist friction meter. It should be observed that the variation of the measured quantities cannot be made independently. A negative correlation between load, W, and twist length, l, is always obtained. This means that the twist is not ideal, but is tightened by a higher load. The values given here are obtained from measurements of kinetic friction.

Four different pairs of nylon fibers were measured. Their thickness was 3 den., which corresponds to a cross-section radius, R, of 0.965×10^{-3} cm. For each pair of fibers, 36 measurements were made, and the quantities measured were varied by varying the number of turns in the twist and the load applied. The ranges of variation were: for l, 0.28–0.84 cm.; for W, 0.6–7.7 g.; and for F, 0.3–2.4 g. (all ranges given approximately). Table I gives the results of the multiple regression analysis based on equation (14), including the rest term obtained, Δ.

The goodness of the fit is illustrated in Table II by the partial coefficients of correlation.

Seven Terylene fibers with different diameters were also measured at different loads. The diameter was diminished by boiling in 10% NaOH solution. In that way it is possible to obtain a uniform reduction of the diameter without swelling the fiber [2]. The variation in the radius was from 0.68 to 0.92×10^{-3} cm.

The other ranges of variation were: for l, 0.36–0.58 cm.; for Rl, 2.5–5.2 $\times 10^{-4}$ cm.^{2}; for W, 1.8–9.0 g.; and for F, 0.9–3.1 g.

The calculations gave $\alpha = 0.266$, $\beta = 12.7 \times 10^2$, and a rest term of 0.08. The partial coefficients of correlation were: $r_{FW \cdot (Rl)} = 0.9780$ and $r_{F(Rl) \cdot W} = 0.6348$.

It is obvious from both experiments that a formula of the same general form as equation (14) corresponds well to the experimental results.

The conclusion is that it is rather meaningless to talk about a coefficient of friction between fibers without simultaneously giving the experimental conditions, because the coefficient $\mu = F/W$ varies considerably with load, fiber dimensions, and way of measurement (length of contact line).

The factor α of equation (14) is obviously almost constant for various fibers of the same kind, and also is about the same for nylon and Terylene. The variation in β for the four nylon fibers is probably due to experimental error, because the term βRl contributes considerably less than the term αW to the value of F. It seems certain that β is considerably greater for Terylene than for nylon.

From equations (15) and (15a) it should be possible to calculate the values of s and p_m if a and E are known. If it is supposed that $a = 0.78$ and the modulus of elasticity of nylon $E = 3 \times 10^5$ g./cm.^{2}, we obtain from the experimental values of the nylon fibers $s = 0.6 \times 10^5$ and $p_m = 2.3 \times 10^5$ g./cm^2. Remember that s is a measure of the strength of material in the welds and p_m is a measure of the yield pressure of the material. It must be kept in mind that the theoretical deduction is approximate, and therefore only the order of magnitude may be discussed.

The strength of nylon fibers is about 4×10^6 g./cm.^{2}, and the strength, s, obtained here is therefore only about 1/70 of that. It might be supposed that the strength of the junction is much lower than the ordinary strength of the material, but it is more probable that the contact is not complete, but is limited to smaller discrete contact areas along the fibers. Therefore, the product As of equation (3) becomes smaller, not so much by a smaller s than expected, but by a smaller A.

The value of p_m is about 1/20 of the nylon strength. The yield limit of a fiber material is not well defined because the plastic and elastic deformations always overlap. If it is considered that the yield limit is only part of the strength and that the fiber strength is measured in the fiber direction, whereas p_m is related to a transverse direction where the material probably yields much easier, the value obtained for p_m seems reasonable.

Since β is greater for Terylene than for nylon, both s and p_m must be greater for Terylene, at least for the samples studied by the authors. We do not think that too much importance should be given to this difference obtained here, because the matter certainly needs more thorough investigation with different types of nylons and polyester fibers. An increase of s might mean an increase of the complete contact proportion of the contact line. A higher p_m means a higher yield limit in the transverse direction of the fiber.

Summary

1. The classical laws of friction of Amontons are are not valid for interfiber friction. The coefficient of friction is not a constant, but decreases in general with increasing load.

2. The interfiber friction is discussed on the basis of the theory of Bowden and Tabor, according to which the force of friction is proportional to the real area of contact.

3. When two fibers are pressed together under a certain load, W, a deformation will occur which is partly elastic and partly plastic. It is possible to deduce theoretically from this assumption a formula for the force of friction, F,

$$F = \alpha W + \beta lR,$$

which shows that the coefficient of friction, $\mu = F/W$, cannot be constant for materials of the kind used in textile fibers, but depends also on the product lR, where l is the length of the contact line and R is the fiber radius. The factors α and β are constants which are related to the elastic and plastic properties of the material.

4. It is shown that the theoretical relation obtained gives a good description of experimental results obtained for nylon and polyester fibers.

5. From the experimental results the values of α and β are calculated and related to the shear strength, s, and the yield pressure, p_m, of the material. It is shown that the values obtained are of the right order of magnitude.

Acknowledgment

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Mechanical Properties of Cotton Fibers

Part III: Effect of Alkali Hydroxide on Fibers Under Tension*

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ALKALI HYDROXIDE solutions acting on cotton fibers under axial tension cause structural changes, as shown by the modified mechanical properties of the fiber. Stress relaxation curves for singly stressed cotton fibers were studied because they, together with stress-elongation curves, characterize closely the mechanical properties of a material [8]. Under the initial test conditions (water-submerged fiber) successive fiber elongation followed by relaxation gave relaxation curves which were identical within experimental error. Relaxation curves were measured and interpreted for the respective reactions of sodium, potassium, and lithium hydroxide solutions. The effects of these reagents on cotton fibers were of added interest as the experimental conditions were similar to those achieved during the mercerization of cotton.

Experimental

The instrument and methods used were identical to those reported in Part I of this series [5]. The method of obtaining relaxation curves for fibers immersed in alkali hydroxide solutions was the same as that reported for studying the effects of acids on cotton fibers under tension [6].

A brief description of the experimental technique used in getting the relaxation curves for singly tested cotton fibers along with a typical data curve to be used as an aid in understanding the experimentally measured curves follow.

The fiber was prepared for testing by attaching one end to a small glass hook and the other end to a small wire hook by means of an acryloid resin (Rohm & Haas A-10). It was then submerged in distilled water at room temperature for at least 48 hrs., care being taken that no tensile force acted on the fiber during this time. In the force relaxation experiments the fiber's length was measured, and then the fiber was mounted within the reaction chamber and attached by its wire hook to a stirrup sitting on a knife-edge affixed to the balance beam.

Measurement of the singly mounted fiber under the various test conditions may be described with the use of a typical autographic data curve (Figure 1). The following sequence of operations was employed. The fiber submerged in water was elongated at a constant rate of 0.0717 cm./min. until some arbitrary force was reached. This is shown by the curve between *A* and *B*. From *B* to *C* the force relaxation curve (at constant fiber elongation) is recorded. At point *C* the water was removed and the appropriate alkali hydroxide solution was pipetted into the reaction chamber. The rapid force relaxation that occurred during this operation, called the "instantaneous relaxation" [6], is rep-

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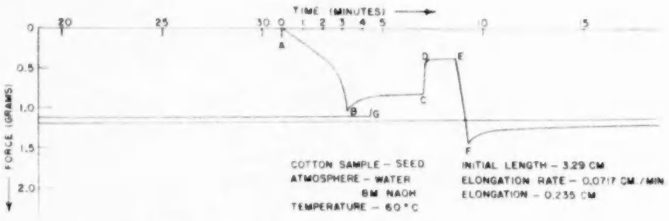

FIG. 1. *Typical autographic data curve.*

resented by the curve between points *C* and *D*. When the time rate of change of the curve between *D* and *E* was of the same order as that of the latter portion of the curve between *B* and *C*, the fiber was re-elongated at the same rate as before until a slightly larger force was supported by the fiber than that at the end of the initial elongation. The relaxation curve in alkali at fixed fiber elongation was then obtained, as shown between *F* and *G*.

These investigations were conducted on seed cotton fibers from the same stock as used in the previous work [5, 6]. It was Upland Cotton Strain No. 234 (grown at Las Cruces, N. M., 1949; grade, Strict Middling or Good Middling).

Alkali solutions of sodium, potassium, and lithium hydroxides were used. Solutions were prepared at the following concentrations: 0.5, 1.0, 2.0, 3.0, 4.0, and 6.0 molal. Three or more curves like Figure 1 were obtained at each of the fixed concentrations of alkali and at each of the temperatures 0°, 20°, 25°, 40°, and 60°C. Additional curves were obtained at other concentrations and temperatures of particular interest. Baker's or Mallinckrodt's analytical-grade reagents and distilled water were used in the preparation of the alkali hydroxide solutions. The solutions were prepared in concentration units of molality with a precision of ±1%.

TABLE I. RELATIVE FORCE REDUCTION DETERMINED FROM INSTANTANEOUS PORTION OF CURVES FOR FIBERS IMMERSED IN NaOH

Concentration of NaOH (molality)	Mean ionic activity of NaOH*	Relative force reduction ($\Delta f/f$)
0.50	0.35	0.03
0.60	0.41	0.04
1.00	0.68	0.08
1.32	0.90	0.10
2.00	1.40	0.16
2.80	2.10	0.24
3.00	2.32	0.25
4.00	3.55	0.34
4.41	4.15	0.38
6.00	8.01	0.47
6.25	8.56	0.48

* Harned, H. S., and Owen, B. B., "The Physical Chemistry of Electrolytic Solutions," New York, Reinhold Publishing Corp., 1943.

Results

Two portions of the data curve shown in Figure 1 best reflect the effect of alkali on the mechanical properties of the fibers. These are the portion between *C* and *D*, designated as the "instantaneous relaxation" section, and the portion between *F* and *G*, called the "relaxation curve after re-elongation in alkali." Since these two parts of the curve are of a different character and represent fiber behavior under different test conditions, they are treated separately.

The instantaneous relaxation of the force on the fiber occurred as rapidly as the alkali hydroxide was added to it, and was complete by the time the fiber became entirely immersed in the alkali solution. With the present experimental arrangement it was impossible to measure accurately the time needed for completion of this rapid effect of the alkali on the fiber, although immersion occurred in less than ½ min. The amount of instantaneous relaxation was extremely sensitive to the concentration of the

TABLE II. RELATIVE FORCE REDUCTION DETERMINED FROM INSTANTANEOUS PORTION OF CURVES FOR FIBERS IMMERSED IN KOH

Concentration of KOH (molality)	Mean ionic activity of KOH*	Relative force reduction ($\Delta f/f$)
0.50	0.36	0.09
1.00	0.76	0.15
2.00	1.80	0.29
3.00	3.26	0.42
4.00	5.41	0.55
6.00		0.58

* Harned, H. S., and Owen, B. B., "The Physical Chemistry of Electrolytic Solutions," New York, Reinhold Publishing Corp., 1943.

alkali solution and independent of the temperature within the temperature range of 0° to 60°C. Even at the higher alkali concentrations where the instantaneous force relaxation was the greatest, the effect of the alkali was such that none of the fibers tested were observed to break. This was in contrast to the effect of acids on the stressed fibers, where the higher concentrations of mineral acids caused the fibers to break during the addition of the acid.

The amount of instantaneous force relaxation at a given alkali concentration was a function of the force supported by the fiber just prior to the addition of the alkali solution. In order to compare curves for the different fibers the "relative force reduction" was calculated. It is defined as the quotient of the amount of the instantaneous force relaxation observed on the addition of alkali, Δf, represented by the distance between points C and D in Figure 1, divided by the force supported by the fiber just prior to the addition of the alkali, f, represented by the vertical distance from A to D. Repeated measurements of the relative force reduction, $\Delta f/f$, at a given concentration and temperature were in agreement within $\pm 1\%$. Relative force reduction values for seed cotton fibers measured at 25°C and at various concentrations of sodium hydroxide and potassium hydroxide are given in Tables I and II.

Graphical representations of the relative force reduction *versus* the concentration of sodium hydroxide and potassium hydroxide, respectively, are shown in Figure 2. These curves indicate that the relative force reduction tends to approach a limiting value at the higher concentrations of alkali hydroxides. This tendency is more evident when the relative force reduction is plotted *versus* the mean

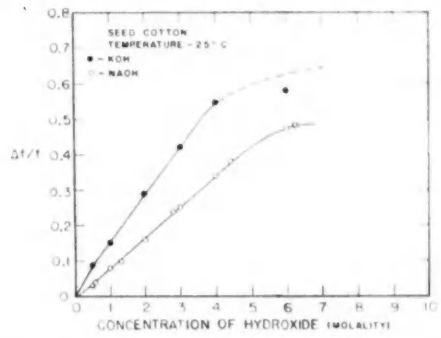

FIG. 2. *Comparison of curves of relative force reduction* versus *concentration of alkali.*

ionic activity of the alkali hydroxides, as shown in Figures 3 and 4. Figure 2 shows that potassium hydroxide causes a greater relative force reduction than sodium hydroxide at any particular alkali concentration (molality). Lithium hydroxide accounts for an even smaller force reduction than sodium or potassium hydroxide. The relative force reduction for these alkali hydroxides varies inversely as the degree of hydration of the alkali cations [4]. The more the alkali ion is hydrated, the less it is able to penetrate the cotton fiber's structure.

From the above curves it is apparent that the alkali hydroxides react with the molecules in the stressed fiber and cause the instantaneous force reduction presumably by breaking certain bonds that support the load. The total force reduction was proportional to the most concentrated solution used, and was independent of the order or number of additions of alkali solution to the fiber. The broken bonds, even after removal of the alkali, are

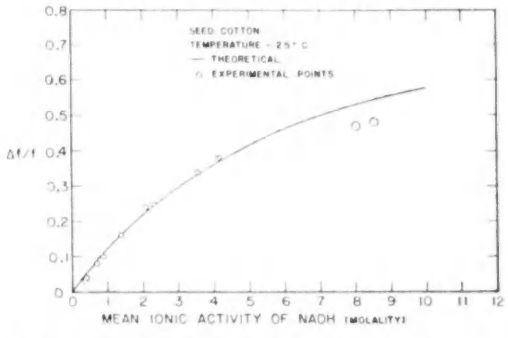

FIG. 3. *Force reduction ÷ initial force from curves of instantaneous effect of NaOH solution.*

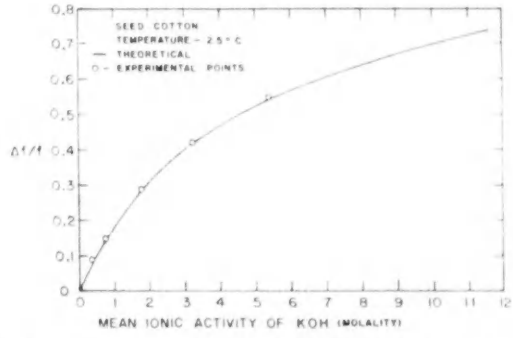

FIG. 4. *Force reduction ÷ initial force from curves of instantaneous effect of KOH solution.*

unable to move back against the force to assume their original positions, but combine with the new neighbors in a relaxed position. From the nature of the reagents and the rapidity of the reaction it appears that the bonds which are attacked by the alkali solutions are secondary valence bonds, probably hydrogen bonds between cellulose chains.

The proposed reaction of the alkali hydroxides with the native cellulose of the stressed fibers appears to proceed until it achieves an equilibrium state. This reaction may be written

$$C_n + MOH \overset{K}{\rightleftarrows} C_n \cdot MOH, \qquad (1)$$

where C_n is the concentration of native cellulosic bonds which support the force on the fiber and are labile to the action of the alkali hydroxides, resulting upon reaction in a reduction of the force supported by the fiber, $C_n \cdot MOH$ is the concentration of cellulose bonds which have reacted with a molecule of the alkali hydroxide, M represents the appropriate alkali cation, and K is the equilibrium constant. The expression for the equilibrium constant for the reaction shown in equation (1) is

$$K = \frac{(C_n \cdot MOH)}{(C_n)(MOH)}. \qquad (2)$$

In order to relate these quantities to the experimental quantities and thus evaluate the equilibrium constant, it was assumed that the limiting value of the relative force reduction is proportional to the total number of bonds that could react with the alkali hydroxides. In terms of the measured quantities, the relative force reduction, $\Delta f/f$, is considered to be proportional to the number of bonds that have reacted with the alkali hydroxides at equilibrium. Using these relations, equation (2) becomes

$$K = \frac{\Delta f/f}{(\Delta f_o/f - \Delta f/f)(MOH)}, \qquad (3)$$

where $\Delta f_o/f$ represents the limiting relative force reduction. To the extent that broken bonds reform in an unstressed position, Δf overestimates their true concentration. The results to follow indicate that this discrepancy does not vitiate the analysis. Equation (3) may be written in the form

$$\frac{\Delta f/f}{\Delta f_o/f - \Delta f/f} = K(MOH). \qquad (4)$$

Equation (4) was rearranged to give the following equation, which is used to evaluate the limiting relative force reduction value, $\Delta f_o/f$, and the equilibrium constant, K:

$$\frac{1}{\Delta f/f} = \frac{1}{K(\Delta f_o/f)(MOH)} + \frac{1}{\Delta f_o/f}. \qquad (5)$$

A plot of $1/(\Delta f/f)$ *versus* the reciprocal of the mean ionic activity of the sodium hydroxide is shown in Figure 5. The limiting value for the relative force reduction of unity was evaluated from the intercept of this plot, and similarly the corresponding value of unity was obtained for the potassium hydroxide-treated fibers. The equilibrium constants of 0.14 for sodium hydroxide- and 0.22 for potassium hydroxide-treated fibers were evaluated from the slope of this plot. Using these values for the equilibrium constants and the value of unity for the limiting value of the relative force reduction, the relative force reductions at various alkali concentrations were calculated using a rearranged form of equation (4). These calculated values are plotted as the solid curves in Figures 3 and 4. The experimental points were also plotted on these graphs to give a comparison of the experimental and theoretical results.

The limiting value for the relative force reduction of unity indicates that sufficiently concentrated solutions of alkali were capable of completely relaxing the force on the fiber. From thermodynamics the equilibrium constant is related to the standard (Gibbs) free energy change, ΔF^o, for the reaction by

$$\Delta F^o = -RT \ln K. \qquad (6)$$

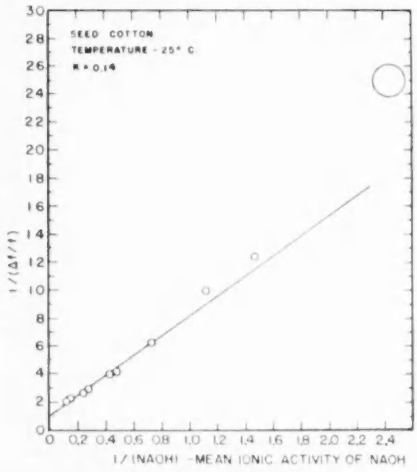

FIG. 5. *Evaluation of* $\Delta f_o/f$ *and the equilibrium constant,* K.

Since

$$\Delta F^o = \Delta H^o - T\Delta S^o, \qquad (7)$$

the standard enthalpy change, ΔH^o, and standard entropy change, ΔS^o, can be evaluated. The standard enthalpy change and standard entropy change accompanying reaction (1) were calculated. ΔH^o was found to be equal to zero since the equilibrium is temperature-independent, and ΔS^o was found to be equal to -3.9 e.u. for sodium hydroxide and -3.0 e.u. for potassium hydroxide.

Comparison of experimental data with theoretically calculated data showed excellent agreement. This supports the explanation of the reaction between the bonds of the cellulose and the alkali hydroxides. The limiting value of the force reduction has been described as being related to the accessibility of the cellulose to the reagent [6]. The value for this quantity of unity indicates that the structure of the cotton fiber is completely accessible to the alkali hydroxide reagents. This is substantiated by x-ray diffraction experiments, which show that alkali hydroxides of sufficient concentration are capable of penetrating and reacting with both the amorphous and the crystalline regions of cotton fibers, resulting in new crystalline lattice dimensions [2, 9]. In terms of the x-ray structure of cellulose, the two concurrent reactions which occur during the time the alkali is added to the fiber are (*1*) the absorption of alkali by the amorphous part, and (*2*) the reaction of alkali with the crystalline part (forming sodium cellulose) [9]. Both of these actions tend to create more amorphous or disordered regions. With these reactions certain of the cellulosic bonds which support the force are released. This leads to the macroscopically observed force reductions.

The typical relaxation curve for a single seed cotton fiber immersed in alkali after re-elongation, shown in Figure 1 between points *F* and *G*, has the same general shape as the corresponding curve for the fiber immersed in water. It was analyzed in the same manner as the curves for air-dried or water-saturated cotton fibers [5]. The nature of this curve indicates that it is a combination of two relaxation processes proceeding at different rates. The resulting empirical equation is

$$F = c_1 e^{-r_f t} + c_2 e^{-r_s t}, \qquad (8)$$

where F is the total force on the fiber at time t during relaxation of the fiber, c_1 and c_2 are constants dependent on the initial loading force on the fiber, and r_f and r_s are the apparent fast and slow relaxation constants for the relaxation processes measured at constant fiber elongation.

The parameters r_f, r_s, c_1, and c_2 were evaluated from the experimental relaxation curves. They were then substituted in equation (8), and data for the relaxation curve were calculated. These are plotted in Figure 6 as the solid curve, and the measured points are shown as small circles. For the relaxation curve zero time was chosen as the instant that elongation or re-elongation of the fiber was stopped. Relaxation curves measured at various alkali concentrations and test temperatures were obtained and analyzed according to equation (8), and the rates r_f and r_s were evaluated graphically. These results are shown in Tables III–VI for sodium hydroxide. The r_f values were found to be approximately 100 to 1,000 times as large as the r_s values. The fast relaxation process, r_f, is complete in the first 5–15 min. of the fiber's relaxation. The slow relaxation has been followed for as long as 400 min., and it was still continuing to decrease at the same rate at that time. The relaxation constants are a function of the temperature and of the concentration of the alkali solution.

These relaxation processes lead to the concept that viscous and elastic elements connected in parallel or in series approximately determine the behavior of the fiber [8]. Such mechanical models are useful because they permit a mathematical treatment of the fiber's behavior. Although there are some objections to their use in crystalline or partly crystalline polymers, they can be used successfully within certain experimental ranges [1].

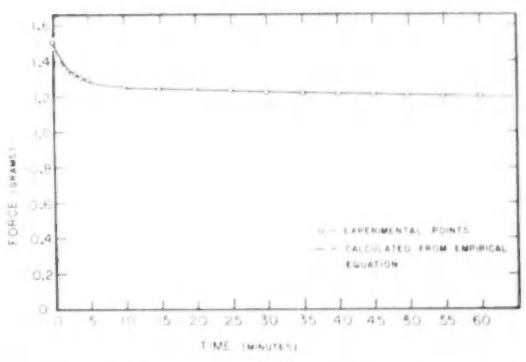

FIG. 6. *Typical relaxation curve after re-elongation of seed cotton fiber in 8M NaOH at 60°C.*

TABLE III. RELAXATION CONSTANTS AND FREE ENERGIES OF ACTIVATION AT 0°C FOR WATER-SATURATED SEED COTTON FIBERS IMMERSED IN SODIUM HYDROXIDE SOLUTIONS

Concentration of NaOH (molality)	r_f (sec.$^{-1}$)	$\Delta F_f^{\ddagger}$ (kcal.)	r_s (sec.$^{-1}$)	$\Delta F_s^{\ddagger}$ (kcal.)
0.00	1.04×10^{-2}	22.21	0.471×10^{-5}	26.39
0.50	1.09×10^{-2}	22.18	0.943×10^{-5}	26.02
1.00	1.21×10^{-2}	22.13	1.61×10^{-5}	25.73
1.50	1.32×10^{-2}	22.08	1.83×10^{-5}	25.66
2.00	1.37×10^{-2}	22.06	2.23×10^{-5}	25.55
2.50	1.44×10^{-2}	22.04	2.70×10^{-5}	25.45
3.00	1.36×10^{-2}	22.07	3.12×10^{-5}	25.37
4.00	1.17×10^{-2}	22.15	3.73×10^{-5}	25.27
5.00	1.11×10^{-2}	22.18	3.53×10^{-5}	25.30
6.00	1.12×10^{-2}	22.17	3.11×10^{-5}	25.37
7.00	1.14×10^{-2}	22.16	3.11×10^{-5}	25.37
8.00	1.19×10^{-2}	22.14	4.73×10^{-5}	25.14

TABLE IV. RELAXATION CONSTANTS AND FREE ENERGIES OF ACTIVATION AT 25°C FOR WATER-SATURATED SEED COTTON FIBERS IMMERSED IN SODIUM HYDROXIDE SOLUTIONS

Concentration of NaOH (molality)	r_f (sec.$^{-1}$)	$\Delta F_f^{\ddagger}$ (kcal.)	r_s (sec.$^{-1}$)	$\Delta F_s^{\ddagger}$ (kcal.)
0.00	1.21×10^{-2}	24.15	2.27×10^{-5}	27.88
0.50	1.30×10^{-2}	24.11	2.48×10^{-5}	27.82
1.00	1.47×10^{-2}	24.04	2.70×10^{-5}	27.77
1.50				
2.00	1.52×10^{-2}	24.02	3.11×10^{-5}	27.69
2.50	1.32×10^{-2}	24.10	3.33×10^{-5}	27.65
3.00	1.20×10^{-2}	24.16	3.11×10^{-5}	27.69
4.00	0.994×10^{-2}	24.27	2.48×10^{-5}	27.82
5.00	0.954×10^{-2}	24.30	2.05×10^{-5}	27.94
6.00	0.911×10^{-2}	24.32	1.83×10^{-5}	28.00
7.00	0.933×10^{-2}	24.45	1.83×10^{-5}	28.00
8.00	1.10×10^{-2}	24.21	2.05×10^{-5}	27.94

TABLE V. RELAXATION CONSTANTS AND FREE ENERGIES OF ACTIVATION AT 40°C FOR WATER-SATURATED SEED COTTON FIBERS IMMERSED IN SODIUM HYDROXIDE SOLUTIONS

Concentration of NaOH (molality)	r_f (sec.$^{-1}$)	$\Delta F_f^{\ddagger}$ (kcal.)	r_s (sec.$^{-1}$)	$\Delta F_s^{\ddagger}$ (kcal.)
0.00	1.23×10^{-2}	25.36	2.48×10^{-5}	29.22
0.50	1.37×10^{-2}	25.29	3.11×10^{-5}	29.08
1.00	1.55×10^{-2}	25.22	3.73×10^{-5}	28.97
1.50	1.49×10^{-2}	25.24	4.34×10^{-5}	28.88
2.00	1.41×10^{-2}	25.28	4.14×10^{-5}	28.90
2.50				
3.00	1.05×10^{-2}	25.46	2.27×10^{-5}	29.28
4.00	0.912×10^{-2}	25.55	1.61×10^{-5}	29.40
5.00				
6.00	0.856×10^{-2}	25.59	1.61×10^{-5}	29.49
7.00				
8.00	0.950×10^{-2}	25.52	1.61×10^{-5}	29.49

TABLE VI. RELAXATION CONSTANTS AND FREE ENERGIES OF ACTIVATION AT 60°C FOR WATER-SATURATED SEED COTTON FIBERS IMMERSED IN SODIUM HYDROXIDE SOLUTIONS

Concentration of NaOH (molality)	r_f (sec.$^{-1}$)	$\Delta F_f^{\ddagger}$ (kcal.)	r_s (sec.$^{-1}$)	$\Delta F_s^{\ddagger}$ (kcal.)
0.00	1.48×10^{-2}	26.86	4.14×10^{-5}	30.73
0.50	1.55×10^{-2}	26.83	5.12×10^{-5}	30.61
1.00	1.73×10^{-2}	26.75	6.03×10^{-5}	30.50
1.50	1.37×10^{-2}	26.91	6.79×10^{-5}	30.42
2.00	1.17×10^{-2}	27.01	6.43×10^{-5}	30.46
2.50	1.08×10^{-2}	27.07	4.54×10^{-5}	30.77
3.00	0.944×10^{-2}	27.16	2.05×10^{-5}	31.21
4.00	0.796×10^{-2}	27.27	1.39×10^{-5}	31.47
5.00				
6.00	0.747×10^{-2}	27.31	1.39×10^{-5}	31.47
7.00				
8.00	0.766×10^{-2}	27.29	1.39×10^{-5}	31.47

The proposed mechanical model for the behavior of cotton fibers under the conditions of these tests was the same as that previously used in explaining the relaxation curves for air-dried or water-saturated cotton fibers [5]. It consists of two Maxwell units (one elastic and one viscous element in series) connected in parallel and used in series with another viscous element. The two Maxwell units are active during the measurement of the relaxation curves for the fibers immersed in alkali. The mathematical analysis of this model was identical with that reported previously [5].

The general solution for the two relaxing units is

$$F = Af_1^o e^{-g_1 t/\eta_1} + Af_2^o e^{-g_2 t/\eta_2}, \qquad (9)$$

where F is the total macroscopic force on the fiber, A is the effective cross-sectional area of the fiber, f_1^o and f_2^o are the forces on the Maxwell elements initially, g_1 and g_2 are elastic spring constants, and η_1 and η_2 represent coefficients of viscosity for the

two dashpots. Upon equating the coefficients in equations (8) and (9), the following relationships were obtained:

$$r_f = g_1/\eta_1, \tag{10}$$

$$r_s = g_2/\eta_2, \tag{11}$$

where the designation r_f with the subscript 1 is arbitrary. Further simplification of the equation is possible by applying the theory of absolute reaction rates to the viscosity coefficient [3]. The expression for the coefficient of viscosity is

$$\eta = \frac{\lambda_1 f}{2\lambda k' \sinh (f\lambda_2\lambda_3\lambda/2kT)}, \tag{12}$$

where λ_1 is the distance between layers of moving molecules, f is the force per square centimeter tending to displace one layer of molecules with respect to the other, $\lambda_2\lambda_3$ is the effective area of the moving segment of the molecule, λ is the average distance between two equilibrium positions in the direction of flow, k is Boltzmann's constant, T is the absolute temperature, and k' is the rate constant giving the number of times per second the flowing segment passes over the potential barrier. Also from rate theory and thermodynamics the rate constant, k', can be derived in terms of thermodynamic functions. The free energy of activation for flow across a potential barrier is related to this constant by the equation

$$k' = \frac{\kappa kT e^{-\Delta F^{\ddagger}/RT}}{h}, \tag{13}$$

where κ is the transmission coefficient, h is Planck's constant, $\Delta F^{\ddagger}$ is the free energy of activation for flow over the barrier, and R is the universal gas constant. By solving equation (12) for k', substituting for r_f and r_s the quantities in equations (10) and (11), then substituting the expression on the right of equation (13) for k', and simplifying, one obtains

$$\Delta F^{\ddagger} = -RT \ln \frac{r_f h \lambda_1 f}{2\kappa kT g_i \lambda \sinh (f\lambda_2\lambda_3\lambda/2kT)}. \tag{14}$$

For Newtonian flow, $2kT \gg f\lambda_2\lambda_3\lambda$, whence the hyperbolic sine can be approximated by a series; by substituting and cancelling like terms, the following equation is obtained:

$$\Delta F_i^{\ddagger} = -RT \ln \frac{r_i h \lambda_1}{\lambda^2 \lambda_2 \lambda_3 g_i}. \tag{15}$$

$\Delta F^{\ddagger}$ could be evaluated by approximating λ, λ_1, λ_2, and λ_3 from the unit cell dimensions (minimum values), and values of g_i and r_i obtained, respectively, from the literature and from experimentally measured data tabulated herein. Values for these parameters that were used to evaluate the $\Delta F^{\ddagger}$ terms were as follows: $g_i = 5 \times 10^{11}$ dynes/cm.^{2}, $\lambda_1 = 4.0$ Å. (distance between cellulose chains), $\lambda = 5.2$ Å. (length of anhydroglucose unit), $\lambda_2 = 3.0$ Å. (a distance between atoms), and $\lambda_3 = 4.0$ Å. (c distance between atoms). $\Delta F^{\ddagger}$ values were evaluated using equation (15), and these are given in Tables III–VI for sodium hydroxide-treated fibers.

TABLE VII. ENTHALPIES AND ENTROPIES OF ACTIVATION FROM THE RELAXATION CONSTANTS FOR WATER-SATURATED SEED COTTON FIBERS IMMERSED IN SODIUM HYDROXIDE SOLUTIONS

Concentration of NaOH (molality)	$\Delta H_f^{\ddagger}$ (kcal.)	$\Delta S_f^{\ddagger}$ (e.u.)	$\Delta H_s^{\ddagger}$ (kcal.)	$\Delta S_s^{\ddagger}$ (e.u.)
0.00	1.06	−77.59	6.93	− 71.28
0.50	1.09	−77.31	5.12	− 76.50
1.00	1.16	−76.74	4.13	− 79.27
1.50	0.10	−80.47	3.95	− 79.52
2.00	−0.42	−82.09	3.30	− 81.62
2.50	−0.80	−83.63	1.46	− 87.42
3.00	−1.01	−84.51	3.02	− 97.15
4.00	−1.06	−85.01	−2.70	−102.59
5.00				
6.00	−1.25	−85.76	−2.36	−101.69
7.00				
8.00	−1.43	−86.14	−3.35	−104.65

From the free energy of activation, $\Delta F^{\ddagger}$, the enthalpy, $\Delta H^{\ddagger}$, and the entropy, $\Delta S^{\ddagger}$, of activation for the relaxation processes are calculated by using the standard equation,

$$\Delta F^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger},$$

and these values are tabulated in Table VII. The enthalpy values are smaller than for water-immersed fibers. However, they are within the range of energies for van der Waals' or hydrogen type bonds. The entropy values are more negative than those for water-immersed fibers. The high negative values are explained as possibly being due to the improbability of segments of cellulose molecules becoming properly oriented before viscous flow can occur [5]. These entropy changes are in agreement with the changes occurring within the crystalline structure caused by the alkali.

TABLE VIII. RELAXATION CONSTANTS AND FREE ENERGIES OF ACTIVATION AT 15°C FOR WATER-SATURATED SEED COTTON FIBERS IMMERSED IN POTASSIUM HYDROXIDE SOLUTIONS

Concentration of KOH (molality)	r_f (sec.$^{-1}$)	$\Delta F_f^{\ddagger}$ (kcal.)	r_s (sec.$^{-1}$)	$\Delta F_s^{\ddagger}$ (kcal.)
0.00	1.09×10^{-2}	23.41	1.16×10^{-5}	27.19
0.50	1.19×10^{-2}	23.36	2.48×10^{-5}	26.89
1.00	1.27×10^{-2}	23.32	3.22×10^{-5}	26.74
2.00	1.37×10^{-2}	23.27	4.53×10^{-5}	26.55
3.00	1.23×10^{-2}	23.34	5.31×10^{-5}	26.45
4.00	1.22×10^{-2}	23.34	5.87×10^{-5}	26.40
6.00	1.23×10^{-2}	23.34	6.24×10^{-5}	26.36

TABLE IX. RELAXATION CONSTANTS AND FREE ENERGIES OF ACTIVATION AT 25°C FOR WATER-SATURATED SEED COTTON FIBERS IMMERSED IN POTASSIUM HYDROXIDE SOLUTIONS

Concentration of KOH (molality)	r_f (sec.$^{-1}$)	$\Delta F_f^{\ddagger}$ (kcal.)	r_s (sec.$^{-1}$)	$\Delta F_s^{\ddagger}$ (kcal.)
0.00	1.21×10^{-2}	24.15	2.27×10^{-5}	27.88
0.50	1.34×10^{-2}	24.09	3.33×10^{-5}	27.65
1.00	1.44×10^{-2}	24.05	4.14×10^{-5}	27.52
2.00	1.34×10^{-2}	24.09	4.73×10^{-5}	27.44
3.00	1.18×10^{-2}	24.17	5.12×10^{-5}	27.39
4.00	1.14×10^{-2}	24.19	5.31×10^{-5}	27.37
6.00	1.13×10^{-2}	24.20	5.69×10^{-5}	27.33

The relaxation curves for potassium hydroxide-immersed fibers were treated in the same manner as those for sodium hydroxide. The fast and slow relaxation constants and the free energies of activation are tabulated in Tables VIII–X, and the enthalpies and entropies of activation are found in Table XI. Similar conclusions to those drawn for fibers immersed in sodium hydroxide were arrived at for potassium hydroxide-treated fibers.

Alkali hydroxides had a pronounced effect on the relaxation constants, the greater effect being on the slow relaxation constants. The variation of the fast and slow relaxation constants for sodium hydroxide-treated fibers with the concentration of alkali is shown in Figures 7 and 8. The numerical values are given in Tables III–VI. Qualitatively, the general shapes of the r_f and r_s curves are the same. The various portions of these curves are explained as being due to the properties of the hydrated alkali cations, using the hypothesis of the penetration and swelling of the fiber by the hydrated ions.

At each temperature the change in the relaxation constants may be explained as follows. It is assumed that the change in the relaxation constants is dependent on the degree to which the fiber has been modified by the hydrated cations under the conditions of the test. The reaction or swelling changes the structure, resulting in different relaxation constants. Qualitatively, the rate of relaxation is then proportional to the amount of reaction or swelling within the fiber. At each particular temperature, as the concentration of sodium hydroxide increases, so does the number of hydrated

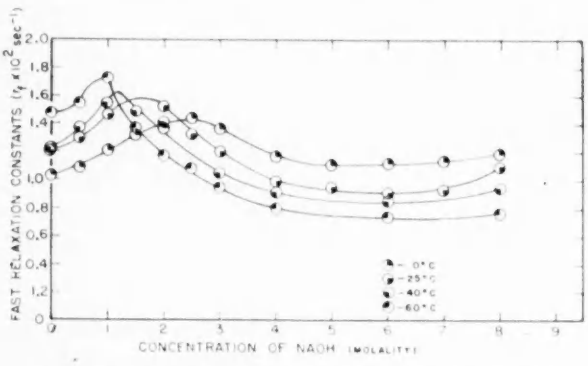

FIG. 7. *Variation of fast relaxation constants with concentration and temperature of NaOH.*

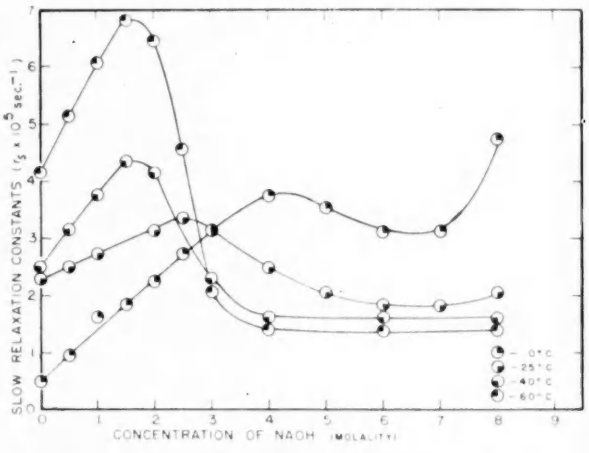

FIG. 8. *Variation of slow relaxation constants with concentration and temperature of NaOH.*

TABLE X. RELAXATION CONSTANTS AND FREE ENERGIES OF ACTIVATION AT 35°C FOR WATER-SATURATED SEED COTTON FIBERS IMMERSED IN POTASSIUM HYDROXIDE SOLUTIONS

Concentration of KOH (molality)	r_f (sec.$^{-1}$)	$\Delta F_f^{\ddagger}$ (kcal.)	r_s (sec.$^{-1}$)	$\Delta F_s^{\ddagger}$ (kcal.)
0.00	1.22×10^{-2}	24.96	2.30×10^{-5}	28.80
0.50	1.40×10^{-2}	24.88	3.74×10^{-5}	28.50
1.00	1.49×10^{-2}	24.84	4.53×10^{-5}	28.39
2.00	1.15×10^{-2}	25.00	4.73×10^{-5}	28.36
3.00	1.09×10^{-2}	25.03	4.93×10^{-5}	28.34
4.00	1.07×10^{-2}	25.04	5.05×10^{-5}	28.32
6.00	1.07×10^{-2}	25.04	5.31×10^{-5}	28.29

TABLE XI. ENTHALPIES AND ENTROPIES OF ACTIVATION FROM THE RELAXATION CONSTANTS FOR WATER-SATURATED SEED COTTON FIBERS IMMERSED IN POTASSIUM HYDROXIDE SOLUTIONS

Concentration of KOH (molality)	$\Delta H_f^{\ddagger}$ (kcal.)	$\Delta S_f^{\ddagger}$ (e.u.)	$\Delta H_s^{\ddagger}$ (kcal.)	$\Delta S_s^{\ddagger}$ (e.u.)
0.00	0.89	−78.09	3.93	−80.54
0.50	1.50	−75.79	3.61	−80.67
1.00	1.60	−75.39	2.89	−82.76
2.00	−1.70	−86.54	0.70	−89.72
3.00	−0.92	−84.11	−1.01	−95.26
4.00	−1.19	−85.11	−1.41	−96.51
6.00	−1.43	−85.92	−1.45	−96.51

cations; this results in an increase of the relaxation rate constants with the concentration of alkali. As the concentration of alkali increases still further, it is assumed that the sodium ions become less hydrated, the size of the entering unit decreases, and swelling and other effects are lessened. This causes a decrease in the relaxation rate for the fiber. It explains the decrease in the value of the relaxation constants for fibers treated with the more concentrated sodium hydroxide. A decrease in hydration of the ions, due to the limited amount of water and the ever-increasing number of sodium ions at the higher concentrations, continues until the sodium ions take water molecules from the water-saturated fiber. This decreases the relaxation constants until they are even less than that for the water-saturated fiber. The degree of hydration of the cations is also assumed to be related to the temperature: the higher the temperature, the less the degree of hydration at a particular concentration. Therefore, the higher the temperature, the lower the concentration of sodium hydroxide at the maxima of the curves in Figures 7 and 8. This explains the displacement with rise in temperature of the maxima in the relaxation constant curves towards lower concentrations of sodium hydroxide.

The variation of the relaxation constants for potassium hydroxide-immersed fibers with concentration of alkali is shown in Figures 9 and 10. In general, the same type of curves were obtained for the fast relaxation constants, and can be explained in a manner similar to those for sodium hydroxide. However, the shape of the slow relaxation constant curve is somewhat different. This may be due to the potassium ion in solution being less hydrated and much smaller in size than the sodium ion. Thus the concentration and temperature effects on the degree of hydration would be less. Also, whereas sodium hydroxide forms a series of apparent compounds with the fiber, the potassium

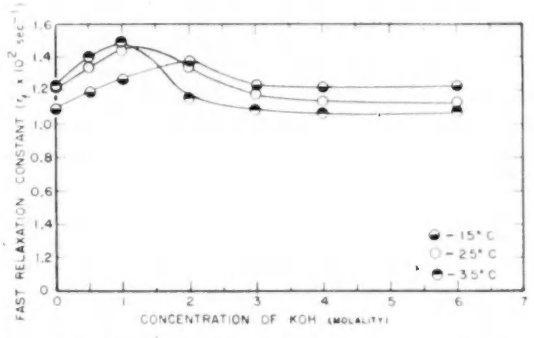

FIG. 9. *Variation of fast relaxation constants with concentration and temperature of KOH.*

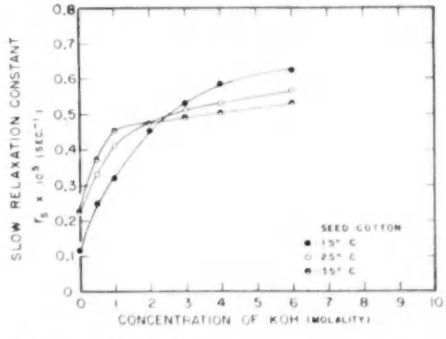

FIG. 10. *Variation of slow relaxation constants with concentration and temperature of KOH.*

TABLE XII. CALCULATED RATE CONSTANTS AND EQUILIBRIUM CONSTANTS FOR POTASSIUM HYDROXIDE-IMMERSED FIBERS AT VARIOUS TEMPERATURES

Temperature (°C)	K (mol^{-1})	k' ($sec.^{-1}$)
15	0.796	6.90×10^{-5}
25	1.216	$5.86 \quad 10^{-5}$
35	2.86	$5.21 \quad 10^{-5}$

hydroxide forms only one compound at concentrations between 17% and 22% potassium hydroxide at room temperature [7].

The curves for variation of the slow relaxation constants shown in Figure 10 show only an increase in the relaxation constant with increased concentration of potassium hydroxide. This increase tends to level off at the higher concentrations. Quantitative treatment of the variation of the slow relaxation constants with concentration and temperature is possible for potassium hydroxide solutions. The potassium hydroxide forms only one compound over the range of concentrations represented by these curves. Its reaction with the fiber may be represented by the equation

$$X_n + \text{KOH} \underset{}{\overset{K}{\rightleftarrows}} X_n \cdot \text{KOH}. \qquad (16)$$

Since the curve approaches a limiting value, it is assumed that this reaction approaches a pseudo-equilibrium. Therefore, the equilibrium expression for the reaction is

$$K = \frac{(X_n \cdot \text{KOH})}{(X_n)(\text{KOH})}, \qquad (17)$$

where K is the equilibrium constant for the reaction shown in equation (16), and X_n is the mole fraction of the native cellulose bonds which are labile to the potassium hydroxide and whose slippage accounts for this part of the relaxation curve. The $X_n \cdot \text{KOH}$ represents the mole fraction of the potassium hydroxide labile bonds which have reacted and have contributed to the relaxation curve. The following equality for the total mole fraction of reactive bonds, X_o, must be obeyed:

$$X_o = X_n + X_n \cdot \text{KOH}. \qquad (18)$$

The relaxation constant is equal to the sum of the rates of relaxation of the native and the modified cellulose bonds:

$$r_s = r_{s,o}(X_n) + k'(X_n \cdot \text{KOH}), \qquad (19)$$

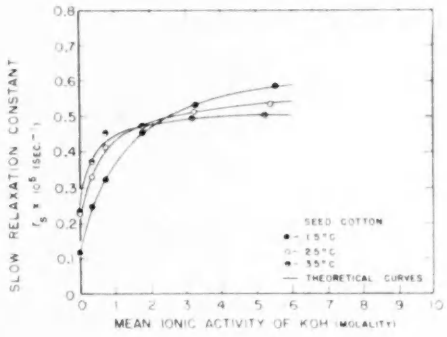

FIG. 11. *Variation of slow relaxation constants with concentration and temperature of KOH.*

where $r_{s,o}$ is the rate constant for the relaxation of the native cellulose bonds for water-saturated fibers, and k' is the rate constant for relaxation of the cellulose bonds modified by the potassium hydroxide. Using equations (17), (18), and (19), the relaxation constant, r_s, is expressed in terms of the mole fraction of labile cellulose bonds. The resulting equation,

$$r_s = \frac{[r_{s,o} + Kk'(\text{KOH})]X_o}{1 + K(\text{KOH})}, \qquad (20)$$

represents the variation of the slow relaxation constant with the activity of potassium hydroxide. Using experimental r_s values from Tables VIII–X and X_o equal to one, the equilibrium constant, K, for the reaction of equation (18) and the rate constant, k', for relaxation of the modified cellulosic bonds by potassium hydroxide were evaluated. These values are given in Table XII.

In Figure 11 a comparison is made between the experimental points and the curves calculated using equation (20) and the values tabulated in Table XII.

The rate constants for the modified cellulosic bonds, k', are higher than those for water-saturated fibers. Thus, their contribution to the relaxation is greater than the contribution from the unmodified bonds. The potassium hydroxide causes disorientation and displacement of the units of the molecular chains, resulting in this faster rate of relaxation.

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(*Manuscript received September 8, 1952.*)

Ethylenimine-Treated Cotton

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Abstract

Raw cotton fiber in the form of card sliver was treated in an evacuated oven with the vapor of ethylenimine. The ethylenimine polymerized in or on the fiber and enhanced its ability to be dyed with acid dyes, but apparently there was little true chemical combination between the imine and the cellulose. Fiber treated in this way, along with appropriate controls, was converted into fabric which was evaluated by various test methods. The results show that cotton may be treated with ethylenimine without adverse effect on the fabric made from it, but, aside from changed dyeing characteristics, no outstanding property has yet been noted for ethylenimine-treated cotton.

DURING World War II considerable work was done in Germany on treating viscose rayon with ethylenimine, apparently for the purpose of changing its dyeing properties so that it could be dyed with acid wool dyes. Although it seems that this work was never published, reports on it were obtained by a British Intelligence team that went into Germany soon after hostilities ceased [1]. Ethylenimine is usually considered to act on cellulose by the formation of a derivative [5], presumably an aminoethyl ether [6], although the German workers were not in agreement on this point. The other possibilities are that the ethylenimine polymerizes in or on the cellulose fibers or that both etherification and polymerization occur. Because of interest in such cellulose derivatives as aminized cotton [7], work has been done at the Southern Regional Research Laboratory on treating cotton with ethylenimine. A portion of this work, details of which will be given elsewhere [3], showed that at least a major part of the ethylenimine polymerized in or on the cotton, since much of it could be removed by dilute acids or by boiling in dilute sodium hydroxide solutions. However, the results of these experiments do not exclude the possibility that some of the ethylenimine actually forms a derivative with the cellulose.

The purpose of the present paper is to describe work in which raw cotton fiber was treated with the vapor of ethylenimine, the fiber then converted into fabric, and the fabric evaluated. Although ethylenimine-treated cotton appears, at present, to have no advantage over untreated cotton except an ability to color with acid dyes, it seems desirable to record this work, especially in view of the German experimentation on rayon, cited above, and because no report of the application of ethylenimine to cotton appears to have been published previously. Although wool dyes are not as fast on the ethylenimine-treated cotton as on wool, some special use for cotton having this unique dyeing property may eventually be found.

* One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

TABLE I

Fabric	Moisture regain (%)	Nitrogen (air-dry basis) (%)	Nitrogen after 6 hrs. kier boil (%)
Ethylenimine-treated	5.94	0.33	0.12
Heated control	6.23	0.11	0.02
Untreated control	6.66	0.12	0.02

Experimental Procedure

Materials

Ethylenimine was prepared by a method which involves flash-distilling a dilute aqueous solution of 2-aminoethylsulfuric acid and sodium hydroxide [8]. Since ethylenimine is a toxic compound, all preparations were made in a fume hood.

The raw cotton card sliver used throughout this experiment was of the Rowden 41B variety, a coarse, thick-walled cotton.

Treatment of Cotton

Thirty-nine pounds of the card sliver was divided into three equal portions. One portion was treated with ethylenimine, another was treated the same as the former but omitting the ethylenimine, and the third was left untreated.

A vacuum oven, 10 in. in diameter and 8 in. deep, was used to make the treatments. The ethylenimine was added by means of a dropping funnel extending into an empty flask inside the oven. Eight-hundred- to twelve-hundred-gram portions of the cotton were placed inside the heated oven and around the flask. After the oven had been evacuated to a pressure of 10–20 mm. of mercury, the cotton was allowed to equilibrate and then the ethylenimine was introduced through the dropping funnel very slowly so that polymerization inside the flask would be at a minimum. The ethylenimine vapor spread throughout the reaction chamber and a uniform treatment was obtained, as demonstrated by removing small samples from different parts of the mass and dyeing with Kiton Fast Red 3GLL, an acid wool dye. Some polymerization occurred on the metal surface of the oven. The amount of ethylenimine added to each batch was equal to 4% of the weight of cotton being treated. Approximately 10% polymerized inside the flask, the remainder being volatilized into the cotton.

TABLE II. RESULTS OF EVALUATION TESTS ON FABRIC FROM ETHYLENIMINE-TREATED COTTON AND FROM APPROPRIATE CONTROL COTTONS

Evaluation tests	Fabric tested: Ethylenimine-treated	Heated control	Untreated control
Thread count (warp×filling)	44×48	45×48	44×48
Weight (oz./sq. yd.)	4.98	4.77	4.72
Thickness (in.)	0.0154	0.0144	0.0146
Strip breaking strength (lbs.)			
Warp	56.4	59.4	62.6
Filling	44.4	46.7	53.2
Tear strength, trapezoid (lbs.)	7.3	7.4	8.2
Cuprammonium fluidity (rhes)	3.2	4.5	2.5
Air permeability (cu. ft.)*	102	115	124
Thermal transmission (% efficiency)†	24.2	21.2	22.7
Wrinkle recovery, Monsanto tester‡			
Warp	103	99	97
Filling	113	88	98

* Gurley Permeometer, $ft.^3/min./ft.^2$ at a pressure drop of 0.50 in. of H_2O [2].

† Method of Tallant and Worner [9].

‡ Federal specifications [4].

The vacuum treatments were allowed to continue overnight for a total time of approximately 18 hrs. at a temperature of 100°–110°C. In most cases the vacuum had dropped slowly until there was little or none at the end of the treatment. The treated cotton was aerated by allowing to stand in a hood to free it of any volatile unreacted ethylenimine. Heat-treated control cotton was prepared in the same way, omitting the ethylenimine.

The three lots—ethyenimine-treated, heated control, and untreated control—were converted into yarn and then into fabric. No difficulties were encountered in drawing, spinning, or weaving these samples. The ethylenimine-treated fabric was yellow in color, while the heated control was light yellow and the untreated control was the creamy white, characteristic of raw cotton.

The ethylenimine fabric dyed much darker with Kiton Fast Red 3GLL or other acid wool dyes than either of the controls. However, these acid wool dyes were not as fast to washing on the ethylenimine fabric as they were on wool. This is in agreement with reported observations on ethylenimine-treated viscose rayon [5].

The results of the chemical analysis of the fabrics are given in Table I.

Evaluations of the fabrics were made by means of standard A.S.T.M. [2] test procedures and equipment unless otherwise stated, and most of the results are given in Table II. It will be noted that the fabric made from the ethylenimine-treated cotton is not much different from the control fabrics with respect to the properties listed in Table II. The fabrics were also subjected to the Taber and to the Wyzenbeck abrasion tests, but no large differences between them were noted. Similarly, no large differences were noted in outdoor exposure up to 1 year or in exposure to light from a carbon arc for 30 hrs. It may be concluded that cotton may be treated with ethylenimine without any adverse effect on its properties. Aside from changed dyeing characteristics, no outstanding property has yet been noted for ethylenimine-treated cotton.

Acknowledgment

Grateful acknowledgment is made to various members of the Cotton Mechanical Processing Division of this Laboratory for the processing of the treated fiber into fabric; to Janice M. Poynot for the testing results; Vidabelle O. Cirino for nitrogen analyses; and Gloria A. Gautreaux for fluidity determinations.

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(*Manuscript received April 13, 1953.*)

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

Supercontraction of Modified Keratin Fibers

HARRIS RESEARCH LABORATORIES
Washington, D. C.
May 29, 1953

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Supercontraction is a phenomenon which has been widely studied in connection with the structure of keratin fibers. It is a spontaneous, and generally permanent, decrease in fiber length which occurs upon treatment with reagents which are able to split various types of bonds such that gross molecular rearrangement occurs [5]. Supercontraction has been noted primarily in the case of reactions which rupture disulfide linkages, such as by reaction with boiling bisulfite solutions [4, 6].

More recently work has been published in which supercontraction was demonstrated with solutions considered primarily as reagents which break hydrogen bonds [1, 2, 5, 7, 8, 9]. While these nonreductive reagents would not be expected to split the disulfide bonds in keratin, nonetheless the conditions under which contraction was observed—prolonged treatment in aqueous systems at elevated temperatures and the use of highly concentrated solutions which produce excessive swelling—make it possible that some splitting of disulfide linkages might also be occurring. In fact, Alexander [1] has reported a small decrease in the cystine content of wool as a result of supercontraction in hot lithium bromide solutions. On the other hand, it has been shown that alkali-treated keratin fibers in which substantial amounts of cystine S have been lost still supercontract in LiBr [1] and phenol [9] at 100°C, suggesting that cystine breakdown is not involved.

As part of a broad study of the reaction of wool and hair with lithium bromide solutions * it was considered desirable to isolate, if possible, the contraction effect produced by secondary-bond rupture from that produced by rupture of the disulfide bond, if, indeed, any of the latter occurs. This possibility occurred to us through a technique previously described in a note from these laboratories [4] in which it was shown that simple replacement of the disulfide linkages in keratin fibers by stable *bis*-thioether linkages results in modified fibers which do not supercontract in boiling bisulfite solutions. This behavior clearly demonstrates the need for disulfide rupture in such a reaction. A modified keratin fiber in which the labile disulfide bonds have been replaced by thioether linkages so that they can no longer participate in supercontraction reactions should be a desirable model substance for evaluating the supercontraction effects of secondary-bond-breaking reagents.

Modified stabilized wool and hair fibers were prepared by a one-step simultaneous reduction and alkylation treatment with sodium hydrosulfite and ethylene dibromide [3]. The supercontraction behavior of these fibers in both a reducing agent, sodium bisulfite, and a hydrogen-bond-breaking agent, lithium bromide, is shown in Table I.

In agreement with our previous findings, the substitution of stable *bis*-thioether linkages completely inhibits the supercontraction of the modified fibers in bisulfite solutions. On the other hand, approximately the same extent of supercontraction is produced by lithium bromide solutions acting on

* Subject of an M.S. thesis by one of us (L.G.B.), Georgetown University, Washington, D. C., 1953 (to be published soon).

TABLE I. SUPERCONTRACTION OF MODIFIED KERATIN FIBERS

Fiber	Modification	Supercontraction (%) in 5% $NaHSO_3$*	Supercontraction (%) in 7*M* LiBr†
Wool	none	28	13
Wool	$Na_2S_2O_4$-$(CH_2)_2Br_2$‡	0	12
Human hair	none	22	9
Human hair	$Na_2S_2O_4$-$(CH_2)_2Br_2$‡	0	13

* Fibers were treated 30 min. at the boil.

† Fibers were treated 60 min. at 80°C.

‡ The fibers were treated along with a piece of wool cloth in a bath containing 0.5% borax (in solution) and 5% sodium hydrosulfite and 10% ethylene dibromide on the weight of the wool. The bath ratio was 30:1, the pH was 9.1, and the treatment was for 30 min. at 95°C. The fibers were then rinsed for 30 min. in running water.

either the untreated or the modified fibers. These results show that unequivocal replacement of the labile disulfide bonds by stable cross-linkages has no effect on the supercontraction produced with lithium bromide at 80°C. Such contraction, therefore, is not a consequence of disulfide breakdown. Analyses of fibers supercontracted in LiBr show little or no change in cystine content, in agreement with these findings.

Any proposed structure for keratin must take into account the inability of intact disulfide bonds to prevent the supercontraction of keratin fibers in reagents which are capable only of rupturing secondary bonds.

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LAWRENCE G. BEAUREGARD
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A Device for Examination of Thickness of a Running Thread

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Kyoto, Japan

December 12, 1952

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The apparent thickness of a running yarn under photoelectric examination for irregularities will be affected by the direction of the passage of the light beam, as shown in Figure 1 (*a* and *b*). This difficulty may be minimized by using illumination with two beams of light following paths perpendicular to each other (*a* and *b* or *a'* and *b'*). When one photocell and a single light source are employed, an optical system using prisms or mirrors is ordinarily required. Figure 2 shows a simpler scheme devised by the authors. A yarn *S* is traversed in contact with a thin glass plate *G*, the under side of which is coated with aluminum or silver. A beam from lamp *L* strikes the plate at 45°. Two parts of this beam, *aa'* and *bb'*,

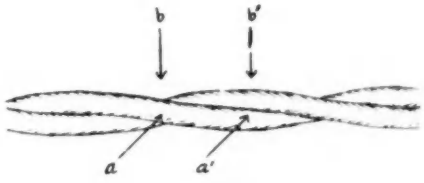

FIG. 1

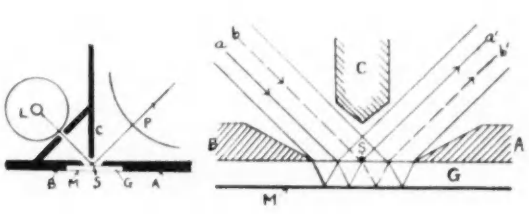

FIG. 2

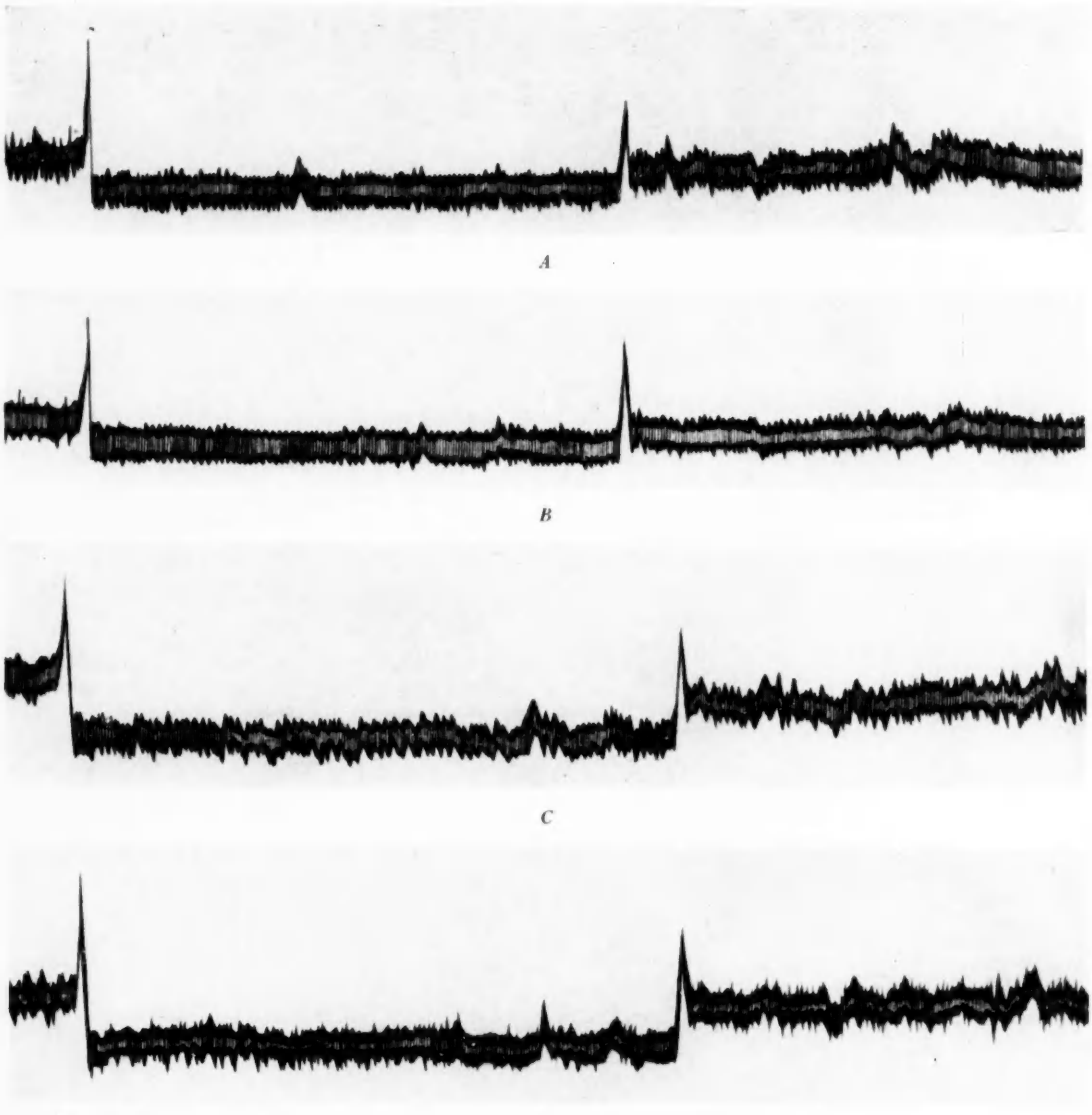

FIG. 3

will pass by the yarn at 90° with each other, the beam *aa'* passing after reflection and the beam *bb'* before reflection from the lower surface of the glass. Both enter the photocell *P*. Since the path travelled by the light is very short, the intensity of illumination is sufficiently great to obviate the use of condensing lenses. The diameter of the running yarn may be read directly on a milliammeter or may be registered on an oscilloscope by using a simple amplifier.

Figure 3 shows results on repeated runs of the same length of yarn (silk). *A* and *B* show the results by illumination in one direction, and *C* and *D* show those of the method described above. It is apparent that there is a greater degree of similarity between *C* and *D* than between *A* and *B*, thus indicating the effectiveness of the method.

SUEKICHI KAWATA
KAORU SEGAWA

Osmotic Active Substances of the Allwörden Reaction

FIBER RESEARCH INSTITUTE T.N.O.
Delft, Holland
April 16, 1953

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The formation of bubbles on the surface of wool fibers when they are immersed in chlorine or bromine water (Allwörden's reaction) depends on the following conditions: (*1*) the epicuticle should be intact to be able to function as a semipermeable membrane; and (*2*) the osmotic pressure of substances that are active beneath the membrane should be strong enough to overcome the opposing forces, which cause the surface layers to adhere to each other.

It seems that the first condition is easily fulfilled, because the epicuticle is very resistant. Although epicuticle protein can be hydrolyzed by the action of strong alkalies at an elevated temperature [7], most practical cases of alkali damage do not show damage of the epicuticle; the retardation of the appearance of the Allwörden bubbles can be explained by a stabilization of the underlying proteins by formation of lanthionine linkages [3]. Oxidizing agents do not attack the epicuticle protein in such a way that the Allwörden reaction is impeded. This is true not only for chloride and bromine, of course, but also for peracetic acid [5], which is known to attack the cystine bonds of proteins specifically. The epicuticle remains intact if the peracetic acid treatment is followed by alkali treatment; therefore, the epicuticle was present in the subcuticle preparations of Alexander [4], although it constituted only a small fraction of the weight of these preparations.

It has been shown [6] that if the Allwörden reaction is followed by alkali treatment, the epicuticle is rapidly dislodged in the form of thin sheets. This proved very useful for microscopic examinations in our laboratory. However, when we tried to increase the yields of our epicuticle preparations by applying this procedure on a larger scale, it appeared that the epicuticle membranes were attacked by hypobromite.

Wool is completely dissolved by sodium hypochlorite [8]; no remnants of the epicuticle could be found by us. It is known that hypochlorite destroys proteins by oxidation of the peptide chains.

These observations lead to the conclusion that the epicuticle protein owes its stability to cross-linkages that are different from those of cystine. It is destroyed, however, by reagents that attack the peptide chains.

The second condition to be met for a positive Allwörden reaction is concerned with the presence of osmotic active substances and with the cohesion of the surface layers. The driving osmotic force being of the same order of magnitude, divergent results can be obtained using different animal fibers and also by using bromine instead of chlorine. Hair specimens of several hundred different mammals were investigated in our laboratory [1], and it was found that in several cases part of the scale layer was lifted together with the epicuticle to form the walls of the bubbles. The observation of Leveau [2] that this happens more readily with bromine water than with chlorine water has been confirmed.

We further investigated the sulfur distribution in material obtained from the interior of the bubbles. Some wool samples were treated with 0.12–0.24*M* bromine water and others with 0.05*M* chlorine water. The solution and washings were combined; they contained the degradation products which had passed the membranes of the Allwörden sacs (fraction *A*). Subsequently the bubbles were destroyed by shaking in water; the substances which were dissolved in the interior of the sacs were contained in the extract (fraction *B*). Finally, the residue of the wool was included in the investigation (fraction *C*). Dry weight, halogen content, *N*, *S*, and cystine were determined. It was found that bromine attacked the wool

TABLE I

	Dry weight (% of original wool weight)	Cystine sulfur (% of total sulfur in each fraction)
Original wool	(100)	92
Fraction *A*		
bromine	22	11
chlorine	18	10
Fraction *B*		
bromine	8.5	53
chlorine	8.5	51
Fraction *C*		
bromine	69.5	23
chlorine	73.5	31

somewhat stronger than chlorine, probably because of its higher concentration. However, in both cases the distribution of the sulfur was found to be similar, as can be seen from Table I.

It can be seen that the osmotic active substances (fraction *B*) still contained more than half of their sulfur in the form of cystine sulfur. This may be the reason why they do not pass through the membrane. Apparently these substances became dissolved by degradation of the peptide chains. In the case of wool treated with peracetic acid [5], however, it seems that the cystine sulfur is the only point of attack. The osmotic active substances dissolve when the pH is raised (the sulfonic acid groups exert a swelling influence). Therefore, the character of the osmotic active compounds differs in each case, but the visible results are almost the same.

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G. J. SCHURINGA
T. KONINGS
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Science Catches Up with an Industry

THE DUPLAN CORPORATION
Kingston, Pa.
July 23, 1953

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

Referring to the article "Properties of Apparel Wools" by Harris M. Burte in the July, 1953, issue of TEXTILE RESEARCH JOURNAL, I was struck by the observation that "when a sample of roving is pulled apart, the fibers on either side of the break tend to be oriented with their tip ends pointing toward the break." The author attributes this to the fact that the coefficient of friction in normal wool fibers is less in the direction of the root-to-tip (with-scale) than in the direction of the tip-to-root (anti-scale). Therefore, when the roving is pulled apart, the fibers tend to move in the direction for which the coefficient of friction is less, and an orientation where a majority of the fibers have their tip ends pointing toward the break must result.

This reminded me of the old method of organizing bunches of hog bristles, which I saw practiced some years ago in a paint factory. As the bundled bristles are received from the Orient, they are opened and laid on a table. The flattened pile of bristles is then oriented so that the butts point in the same direction by the simple trick of placing across the two ends of the package a ruler or other rigid stick, and then slowly moving the sticks apart while pressing tightly on them. This effectively prevents the large butt end of the bristle from moving under the ruler and at the same time permits the small, finely tipped end to move freely. As a result, when the two rulers have fully separated the package, the butts of the bristles are under each of the rulers. The rulers are then swung around so that they are in line and the package is reassembled for manufacture of a brush.

This practical method from a rapidly dying section of the brush industry, which results in the same effect as Dr. Burte's pulling apart of wool rovings and yarns, adds confirmation to the observation that the coefficient of friction, and possibly in the case of bristles the marked taper of the fiber, governs the direction in which the fibers migrate. It adds credence to the old saying, "there is nothing new under the sun."

MARTIN H. GURLEY, JR.

INDUSTRIAL SECTION

Frictional Properties of Filament Yarns and Staple Fibers as Determined by the Stick-Slip Method*

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Tennessee Eastman Company, Kingsport, Tennessee

Abstract

This paper describes instruments for measuring the forces involved in the stick-slip process in filament yarn friction and the forces between staple fibers during drafting. Electrical strain gages and high-speed recording instruments have been incorporated into testing equipment to furnish an accurately recorded measurement of the rapidly fluctuating forces which may occur during motion of yarn or fiber samples. Details of calibration and performance are given, together with typical tests illustrating the wide range of results observed. A simple equation has been employed to assign a numerical value to smoothness of fiber movement. Both static and kinetic values of friction can be obtained from a single stick-slip cycle.

Introduction

Numerous measurements of kinetic friction have been made. Many of the previous studies record only the average forces necessary to maintain sliding. Fundamental investigations of fluctuations in frictional forces have been conducted by several people. Most of this work has involved sliding forces between metal surfaces both dry and lubricated [2, 3, 4, 7, 12, 17]. Bowden and Leben conducted pioneer studies of the basic physical processes which occur during sliding and the nature of the physical force which opposes motion.[7] Experiments have shown that frictional forces are rarely constant in magnitude. They usually undergo rapid and violent fluctuations. The sliding process is not continuous but proceeds by irregular jerks. Surfaces stick together until, as a result of the gradually increasing pull, there is a sudden break, with a very rapid slip. The surfaces stick again, and the same process is repeated indefinitely. This phenomenon has been termed the "stick-slip effect" in the literature. It has been investigated to a limited extent on various fibers [1, 5, 6, 8, 10, 11, 13, 14, 15].

In Mercer's experiments a single fiber, mounted in a bow, was carried forward with a speed of between 0.01 and 0.1 cm./sec. while pressed against a cylindrical piece of ram's horn, or other substance, with the required load. The horn was mounted on a piece of clock spring, the deflection of which, recorded by photographic means using a moving-film camera, was a measure of the frictional force. The stick-slip friction effect was demonstrated on a number of textile fibers.

Vibration produced by the stick-slip effect is illustrated by common everyday experiences—the squeaky hinge, chattering brakes, the shriek of skidding tires, the violin bow. Although this effect is commonly associated with unlubricated surfaces, careful investigations have shown that the stick-slip effect is the rule rather than the exception, even with lubricated surfaces. The fundamental cause of this effect is the difference between the static and the kinetic coefficients of friction. Kinetic friction is much lower in most cases than static friction.

In studies of friction in textile materials, the importance of the static friction has been largely neglected. There are a number of instances where this value is important. For example, if it is too low,

* Presented at a meeting of The Fiber Society at Princeton, N. J., on Sept. 11, 1952.

yarn will tend to slough off a package with a low cross-wind. If it is too high, it may contribute to stretched yarn in filling. An examination of the stick-slip effect helps to provide an insight into the relationship between static and kinetic friction.

There are several obvious shortcomings in some of the methods of measurement described herein. Much work remains to be done. It is hoped that the work reported here will serve to lend emphasis to the importance of static friction and the influence of the stick-slip effect on some of the problems in textile processing.

Stick-Slip Studies in Connection with Filament Yarns

What are some of the problems encountered in connection with the stick-slip friction as evidenced on filament yarn? When continuous-filament yarn is drawn across a surface, as, for example, a needle in a knitting machine, it sets up vibrations due to the nonuniformity of the frictional forces. This effect may be compared with the action of a bow as it produces a musical tone when it causes a violin string to vibrate. In extreme cases in textile processing, yarn passing over needles, guides, fabric, or other surfaces will actually produce such a musical tone, due to the vibrations induced. In the trade, yarn with this characteristic is said to have a "harsh hand"; or it may be described as "scroopy." No device or instrument has been available to the trade to evaluate this property of continuous-filament yarn. Mill men customarily test the yarn by drawing it between the fingers. If there is little tendency for the yarn to vibrate or chatter, it is said to have a "soft hand." Such a technique requires a considerable amount of skill and experience. It suffers other important shortcomings—it is subject to personal errors in judgment, provides no quantitative comparison between samples, and is not sufficiently sensitive to demonstrate small differences. The frictional characteristics of the yarn against the fingers may be, and in most cases are, different from the characteristics observed with yarn running against a guide or yarn against yarn.

In certain cases in processing filament yarn, harshness of hand, producing a high-frequency variation in frictional forces, may contribute to irregularities in the appearance of the finished fabric. For instance, as the reed of a loom beats the filling yarn into the fell of the fabric, harsh or scroopy yarn may cause the picks to be nonuniformly spaced, producing streaks. This condition has been given several names by mill personnel; it has been called "raised picks" and "static cracks." It has been known to contribute to a *barré* condition. This condition is more pronounced in certain types of construction than others. It shows up in taffetas and, to a lesser extent, in marquisettes. It has been proved defi-

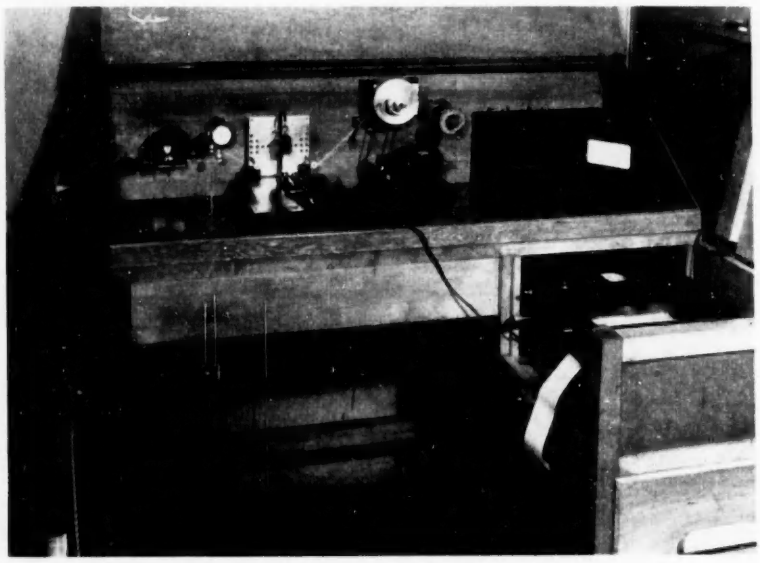

FIG. 1. *Friction analyzer.*

nitely that a scroopy yarn can cause this condition and that a soft finish can help in eliminating it.

Testing the processing qualities of yarn by running weaving or knitting trials is expensive and time-consuming. It does not allow close control over the characteristics of the finish applied as may be necessary to maintain a high standard of quality. It is desirable to be able to evaluate scroop or harshness for quality control of the finish applied as well as to evaluate properties of new finishes.

The device developed at Tennessee Eastman Company to make these tests is illustrated in Figure 1. The operation of the device may be described briefly as follows: Yarn to be tested is drawn, with constant speed and tension, in contact with a short length of music wire, yarn, or other flexible object. Fluctuations in the force of friction against the wire cause it to vibrate or chatter with an amplitude determined by the material and dimensions of the wire, the tension on the wire, the contact force between the yarn and the wire, and particularly the lubricant or finish applied to the yarn. A flat stylus, in contact with the wire, transmits the force to a piezo-electric crystal pickup which converts the mechanical motion to electrical impulses. These electrical impulses are amplified and may be recorded by means of an oscillograph. It has been found preferable, however, to feed the signal through a filter or integrating circuit to an electronic peak value voltmeter.

In order to obtain satisfactory results in testing for fluctuations in frictional forces, it is essential that any variations in speed or tension be held to an absolute minimum. The yarn passes through a pretensioning device which supplies only enough tension to snub the yarn so that it will not slip as it passes around the pulley of the tensioning motor. The yarn is wound around this pulley in such a direction that it causes the intended direction of rotation of the motor to be reversed. The tension of the yarn is regulated by electrically controlling the torque of the tensioning motor by means of two rheostats in series with the motor. This method of tensioning provides a convenient means of regulation and a higher degree of uniformity than can be obtained, at the low speeds necessary, by the more conventional tension controls usually employed in textile processing. The inertia of the tensioning motor aids in eliminating any surges in tension which may have been introduced by the stick-slip effect in the pretensioning device.

The yarn passes around the pulleys of a conventional tensometer, and over a guide pulley, to the transverse flexible unit, which may be composed of any material against which it is desired to test the yarn. As the yarn passes over this guide it changes direction, so as to produce a contact force, and passes over another guide pulley as it proceeds to the drive roll. The synchronous drive motor is geared down to the desired speed. After passing around the drive roll, the yarn is wound onto a take-up roll or spool, where it is retained until it is desired to dispose of the sample.

The piezo-electric crystal pickup is similar to a phonograph pickup except that the stylus is chisel-shaped. The point rests lightly against the wire. A micrometer screw adjustment allows the contact pressure of the stylus to be positioned for maximum sensitivity.

Absolute calibration of this instrument would pose quite a problem. However, this is not deemed necessary. A bobbin of yarn is chosen as a standard, and other samples are compared with this. It has been found possible to reproduce readings within 3% using this comparison method.

This device is limited to tests on continuous-filament yarn. The sample tested must be free of slubs, broken filaments, or other similar imperfections, since the forces measured are of smaller magnitude than those which would be caused by such irregularities. It is desirable, but not essential, that the samples have little or no twist. It is essential that the samples tested for comparison of finishes be chosen so that their other physical properties, such as denier, filament size and count, twist, luster, etc., are identical, since each of these properties influences the results obtained. Again, since the forces to be measured are quite small, it is mandatory that the pickup assembly be shock-mounted so as to isolate this sensitive element from vibrations produced by the motors or any other equipment in the building.

Figure 2 shows oscillograph charts obtained when testing four representative samples. Sample *A* was harsh yarn. Sample *D* was smooth yarn used for comparison. These are the extremes. Samples *B* and *C* illustrate yarns with intermediate values of scroop. It should be pointed out here that the natural frequency of the wire is superimposed on and influences the frictional pattern which actually is characteristic of the yarn. It was found to be quite

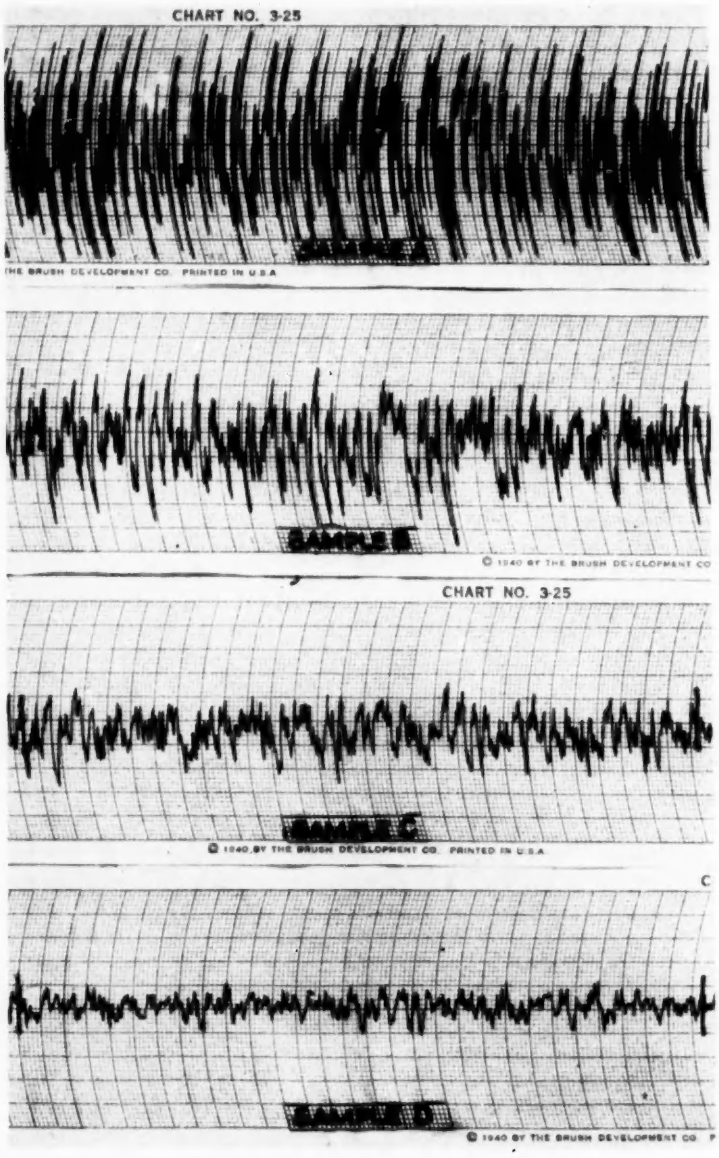
CHART NO. 3-25
THE BRUSH DEVELOPMENT CO. PRINTED IN U.S.A.
SAMPLE B
© 1940 BY THE BRUSH DEVELOPMENT CO
CHART NO. 3-25
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C
© 1940 BY THE BRUSH DEVELOPMENT CO. P

FIG. 2. *Yarn friction analysis.*

tedious to evaluate charts, such as those shown here, for quantitative comparisons. Consequently, a method was developed for obtaining the average value of this vibrational energy level.

The signal was rectified and fed through an electrical low-pass filter circuit with a long time constant. This may be loosely termed an "integrating circuit." When connected to a suitable indicating or recording meter, it amounts to an electronic A.C. voltmeter designed to respond to the low frequencies involved. A recorder was run at a much slower speed, charts representing results obtained on

yarn specimens several hundred times as long as those shown in Figure 2. In some cases, variations in vibrational energy level have been found to be periodic and related to the wind pattern or the method of lubrication.

In case a recording meter is not available, similar results may be obtained by using any good high-resistance indicating meter and taking an average of ten or more readings spaced over several minutes. However, the charts are relatively easy to compare and evaluate, and have the additional advantage of making it easier to discover unusual trends and cyclic variations.

Data obtained from tests of the type just described have aided materially in discovering causes contributing to a number of problems in processing textile fibers.

A Second Stick-Slip Friction Tester for Yarn—The "Slow-Speed" Yarn Tester

As a background of experience was acquired in studying friction on yarn, the need became apparent for a test which would allow each individual stick-slip cycle to be analyzed more thoroughly. The so-called "slow-speed friction tester" was developed (Figure 3). Here the individual forces actually are measured by means of a resistance wire strain gage commercially known as a Statham gage [16]. The yarn is drawn through the device at a speed of only 1 in./min. by a synchronous clock motor (not shown in the picture). Tension is applied by gravity by means of a suitable weight after the yarn passes over a pulley. The yarn guide, by means of which the friction is applied, is composed of five cylinders about $\frac{3}{16}$ in. in diameter. The top of the guide assembly, holding the second and fourth cylinders, is hinged so that it opens up in order to allow the yarn to be placed in position. When the top is closed the yarn runs over the first cylinder, under the second, over the third, and so on. The cylinders are placed so as to produce a deflection in the yarn of about 10 degrees at each contact. Polished steel, porcelain, and several types of Alsimag have been used to make up the cylinders.

The guide assembly is mounted at the top end of an aluminum lever, the lower end of which is attached to a hub mounted in high-quality miniature ball bearings. The force on the lever is sensed by means of the Statham gage. The gage used has a

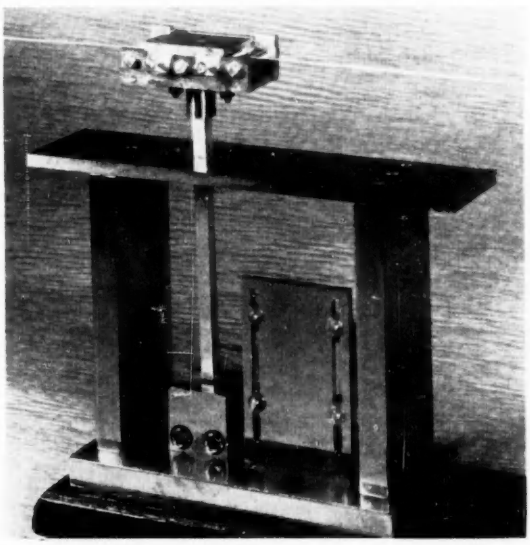

FIG. 3. *Slow-speed friction tester.*

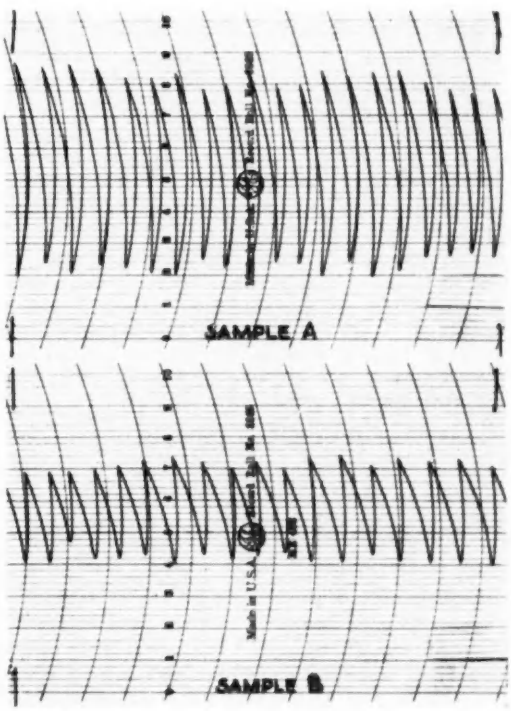

FIG. 4. *Slow-speed friction analysis.*

sensitivity of 4 oz. with a displacement of only 0.0015 in. The gage may be raised or lowered to obtain the required lever ratio and calibration. The resulting sensitivity is approximately 2 oz. or 50 g. full scale. Absolute calibration may be checked by using known weights attached to a length of yarn run over a pulley. Fine calibration adjustment is made by means of a rheostat in the battery circuit supplying the gage.

In Figure 4 is shown the type of chart obtained from tests on yarn when the instrument is used. The first chart illustrates the stick-slip effect produced by the same scroopy yarn used in previous tests. The lower chart is the result of tests on a moderately harsh yarn. The saw-tooth type of curve is well defined. It must be remembered that a slight degree of distortion is introduced due to the fact that the chart presentation is not strictly rectilinear. However, the gradual build-up in force followed by the sudden slip, repeated in uniform cycles, is readily apparent. Note that the minimum force in each cycle in sample *A* is only approximately one-fourth that at the maximum in each cycle. Each chart division represents 1 g. of force. It is interesting that conventional tests on kinetic friction of this particular yarn show that running friction at normal processing speeds is lower than that found with commercially available yarns.

Yarn samples which are available commercially ordinarily exhibit an average level of frictional force of the order of 15 to 20 g. when tested under these conditions. Variations usually do not exceed about 10% of the mean value. Maximum or minimum values observed during a long series of these stick-slip cycles usually exhibit a remarkable degree of uniformity. Few peak values which differ by more than 5% of the average maximum are ordinarily observed, even in charts representing several hundred cycles. Among the hundreds of types of yarn lubricants tested, only a very few samples have been found in which the stick-slip effect is either insignificant or nonexistent at these slow speeds.

The coefficient of friction is directly proportional to the force in grams shown on this instrument. The coefficient, to a close approximation, may be obtained by dividing the force in grams by 100. The coefficient of starting or static friction in sample *B*, then, is about .35, and the coefficient of kinetic friction is about .21. The ratio between the coefficient of kinetic friction and the coefficient of static friction has been used as a figure of merit for the smoothness of the yarn. When multiplied by 100, to yield a whole number, this is called the "smoothness factor." For sample *B* this factor is $S = 100 \times .21/.35 = 60$. Another way of stating this result is to say that 60% of the maximum force remains at the end of the slip. Using this terminology, a sample would be said to have a smoothness factor of 100 if no sudden slip were involved.

The authors realize that strict use of the "trough" load value as a measure of dynamic friction might be open to question. However, errors introduced by the response of the recorder and the change in momentum of the system appear to be of minor importance. Tests covering dynamic friction have been carried out with the yarn running at a wide range of different speeds, from a few inches per minute up to a maximum of several hundred feet per minute. Dynamic friction usually varies with speed; "trough" load values observed in stick-slip tests correspond to dynamic values for the slower speeds. The yarn was moving 1 in./min. in the tests illustrated. Each chart division represents 10 sec. Similar stick-slip tests have been made with the yarn moving as slow as 1 in./hr. The frequency with which the cycles are repeated is influenced by several factors, the most important of which are the speed and elasticity of the yarn and the distance from the friction element to the drive roll.

Before leaving this phase of the subject, it may be appropriate to make a few basic generalizations: (*1*) Other things being equal, bright yarn has higher chatter and higher average friction than dull yarn. (*2*) Brightly polished guides cause higher friction and more chatter or scroop effect than guides which have a satin or velvet finish. As the latter type of guide is worn smooth, the friction increases. (*3*) The frictional characteristics of filament yarn are determined primarily by the finish applied. Charts or tables showing values of friction and simply identifying the yarn as viscose, acetate, nylon, etc., are essentially meaningless, since a single type of yarn can be lubricated so as to exhibit any of the characteristics discussed above.

The Stick-Slip Effect as Observed in Interfiber Friction of Staple Fibers

A most important phase of the study of the friction of fiber against fiber is encountered in the investigation of forces involved when roving is drafted

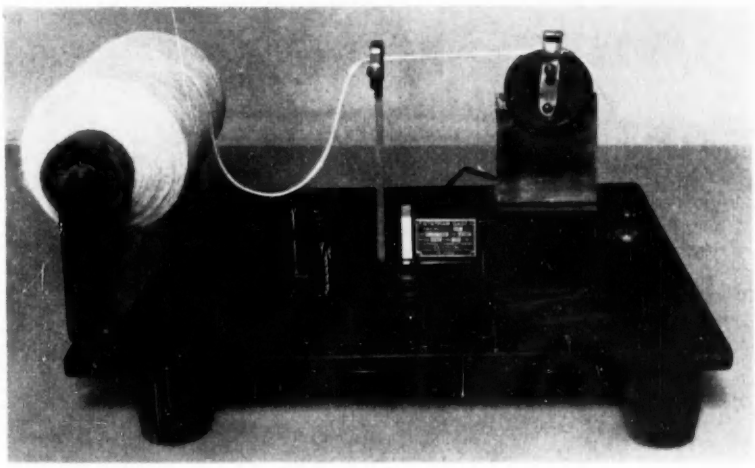

FIG. 5. *Single draft roving tester.*

[9]. The frictional forces existing between the component fibers of sliver, roving, or yarn are factors which influence the fineness and uniformity of yarn which can be drawn as well as the "hand" or feel of a finished fabric. Many people in the textile trade believe that finishes which do not minimize irregular fluctuations in frictional forces will cause or contribute towards uneven drafting, which will produce an irregular yarn and an inferior fabric.

Heretofore, it has been necessary to judge the nature of interfiber friction by the sense of touch or feeling. One technique involves squeezing a handful of the fiber. The crunching effect of a harsh finish can be felt easily. When the fibers are held near the ear, a definite sound is produced similar to that which is sometimes heard when walking through snow. Others test a sample of roving by slowly breaking it by hand. Although such tests doubtless have merit when made by an experienced operator, they do not lend themselves to precise measurements.

A device to analyze the forces involved as roving is slowly broken is shown in Figure 5. Roving is drafted by means of a timing motor whose shaft turns $\frac{1}{3}$ r.p.m. The diameter of the grooved take-up pulley was designed to provide a drafting rate of 2 in./min. A spring loaded clamp attached to the side of the pulley secures the moving end of the sample. A clutch on the motor shaft allows the clamp to be started from the same position for each test. The fixed end of the roving is clamped to the top end of a lever which is pivoted at the bottom. A Statham gage is positioned against this lever in an arrangement similar to that shown with the slow-speed friction tester. The roving clamps are spaced 4 in. apart. A 48-oz. gage is used. The location of the gage may be adjusted by means of a spacing block to give either 200 g. or 400 g. full scale.

Typical charts obtained from this test are shown in Figure 6. The charts are representative of five general groups: (*1*) saw-tooth patterns with an appreciable recorder overshoot at the end of the slip, as illustrated in chart *A*; (*2*) saw-tooth patterns with only moderate overshoot, as shown in chart *B*; (*3*) saw-tooth patterns without overshoot, as in chart *C*; (*4*) sinusoidal fluctuations, following curved rather than angular inflections, as represented in chart *D*; (*5*) smooth curves with no appreciable stick-slip effect, as in chart *E*.

Chart *F* represents an unusual sample. At the top of each cycle, drafting appears to occur smoothly for a short distance. Then a sudden slip occurs with a considerable amount of recorder overshoot. Only one lubricant studied yielded this type of behavior.

Numerical evaluation of the fiber characteristics portrayed by these charts may be made in a number of ways. The method found to be the most satisfactory is similar to that described for the slow-speed friction tester. The maximum slip is selected. The force is read from the chart at each end of this line. The smoothness factor, S, is defined as $S = 100 \times \text{minimum force} \div \text{maximum force}$. Stated in

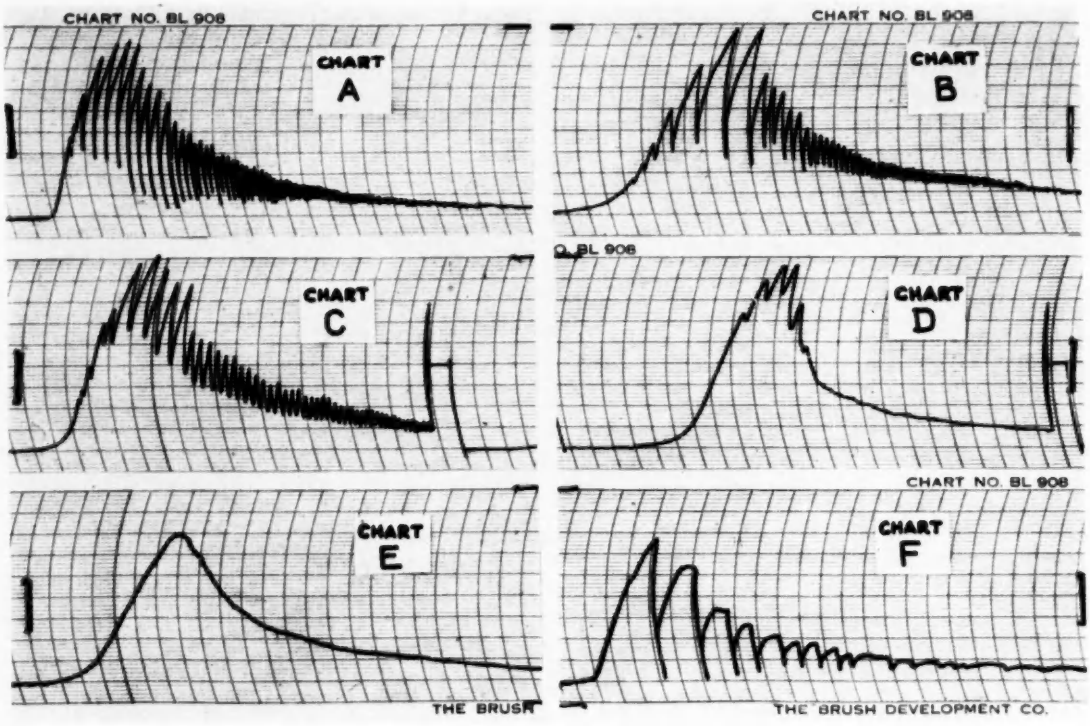

FIG. 6. *Single draft roving analysis.*

a different fashion, the smoothness factor is the percentage of the tension remaining at the end of the slip. Results obtained from this equation have proved to be quite constant when tests are repeated on the same sample. Sample *E* would be rated as having a smoothness factor of 100. One characteristic observed in the charts which is not brought out by this simple equation is the relative speed with which slips occur.

The degree of overshoot by the pen gives an index to the speed with which the force relaxes. The recorder has a linear response from zero to 100 cycles/sec. An appreciable overshoot indicates very rapid change. The magnitude of the stick-slip variation shown in chart *A* is of the same order of magnitude as that shown in chart *C*, yet the overshoot in *A* is as great as the remaining part of the cycle. Each transverse chart division represents 1 sec.

The properties imparted by a fiber finish usually are the result of a compromise which involves several physical properties. Each finish used commercially has its own particular advantages. The fiber represented in chart *A*, as a result of its higher friction, requires somewhat less twist to produce a given roving strength than that represented by charts *D* and *E*. On the other hand, although the latter two finishes impart a smooth drag to fibers during drafting, some additional twist may be required.

Four basic properties other than finish must be taken into consideration when analyzing charts obtained on roving tests: staple length, fiber stiffness, roving twist, and luster.

Other things being equal, a short staple length minimizes the stick-slip effect, but a staple length of 5 or 6 in., as obtained with the Pacific Converter process, gives a pronounced stick-slip effect even with a soft finish. A stiff fiber produces a curve with a lower smoothness factor, regardless of whether the stiffness is the result of difference in denier per filament or a material with different elastic properties. In some cases, when the twist is higher than normal, a finish which usually exhibits

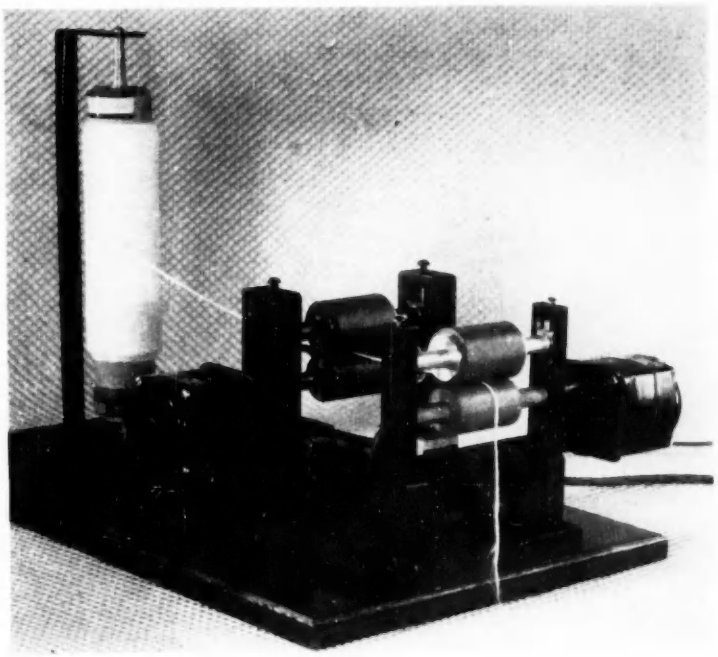

FIG. 7. *Continuous draft roving tester.*

a smooth drag will show a single slip of considerable magnitude with no subsequent recovery in strength. Dull staple exhibits a higher smoothness factor than bright staple. Due to its limited use, very little bright staple has been evaluated by this test, but this result is in agreement with observations made on the frictional properties of bright continuous-filament yarn.

A Continuous Roving Tester

As a result of the information obtained by drafting short sections of roving, it was considered that additional knowledge could be gained by applying the same technique to studies under dynamic conditions such as occur in mill operations. Moreover, since for a given fiber stock the drafting force would be proportional to the number of fibers present in the cross section, measurement of the drafting force probably would serve to indicate the degree of uniformity of the cross section of the roving—that is to say, evenness.

Drafting usually is accomplished by three pairs of drawing rolls with a draft in the range of 3 to 10, depending upon the type of staple being run and the equipment being used. The original development work with two stages of drafting using three sets of rolls was unsuccessful. In order to obtain complete measurement of the forces involved, it was found necessary to resort to a single stage of drafting at a low draft ratio in the neighborhood of 1.33:1 and at slow speed. The machine finally developed is shown in Figure 7. The front roll system is suspended from a balanced pivoted frame, the pivot serving as the fulcrum for the drafting force applied to a Stathan strain gage through the frame as roving is drafted. The rolls are driven directly by means of small synchronous gear motors. Drafting forces and their fluctuations are translated by the strain gage into electrical energy, which in turn is measured and recorded continuously, utilizing a G.E. recording microammeter. The front drafting roll is direct-connected to the 2 r.p.m. motor and the rear drafting roll to the 1.5 r.p.m. motor; the surfaces of both rolls are serrated or fluted to avoid slippage of the fibers during drafting. The pressure rolls are rubber-covered. Pressure is applied through the bearings by means of screws at each end of the pressure roll shaft. Spacing between front and rear rolls may be adjusted to accommodate different fiber lengths. In general, the rule followed is

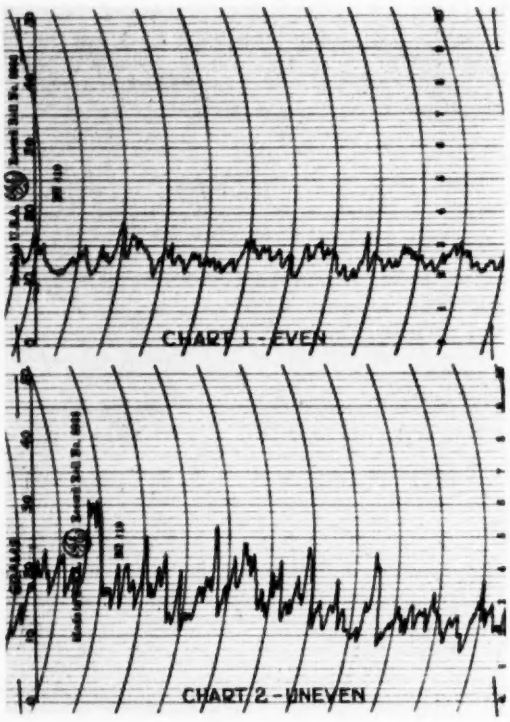

FIG. 8. *Continuous draft roving analysis.*

to allow spacing between rolls equal to the length of the staple plus $\frac{1}{4}$ in. The tester may be calibrated so that the drafting forces in grams may be read directly from the recorder chart.

As in the case of the original roving tester, the results from the continuous tester may be expressed as a smoothness factor, this being a ratio of the minimum to maximum forces encountered during drafting. As before, factors of fiber lubrication, staple length, fiber stiffness, roving twist, and fiber luster must be considered in the analysis of the data.

One very important problem encountered in the development and construction of the machine was that of the elimination of background or extraneous vibrations associated with the driving units and the support. This effect was reduced to less than 5% of the total force involved. In Figure 8 are shown typical results obtained when drafting rovings with different finishes, the top chart being that from a roving having a relatively soft finish and the bottom chart being that of a roving having a harsher or scroopy finish. These charts also illustrate the range of forces encountered in a drafting process of this type.

The continuous roving tester has been utilized in the study of interfiber friction forces encountered in drafting in connection with fiber lubrication studies. The tester also has been used to advantage in the analysis of mill problems involving unsatisfactory roving and yarn uniformity.

Conclusions

Although the instruments described herein do not yield data that are easily analyzed except in a qualitative manner, the tests have proved to be both sensitive and reproducible. The measurements are all adapted to rapid routine testing of a large number of samples employing relatively unskilled personnel. Despite the shortcomings of the techniques described, they have been found to be virtually indispensable for evaluation of new fiber lubricants. The tests have rendered valuable aid in solving a number of elusive problems in processing.

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Balloon Diameters and Thread Tensions Calculated for Different Cap-Spinning Conditions

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Introduction

The shape and tension of the ballooning thread in a cap-spinning system depend on various technical features, such as the dimensions of the spinning frame and the properties of the yarn. The present paper describes the results of a theoretical investigation of the effects of balloon height, cap radius, bobbin radius, bobbin speed, and yarn denier on the shape and size of the balloon and on the tension in the yarn at the bobbin and just below the top guide.

This is a sequel to an earlier paper [1] in which the influence of thread tension on balloon profiles in air and in vacuum was discussed. There, thread tension just below the top guide was taken as a parameter to be chosen, but in practice it is, of course, determined by the conditions of spinning. It is, in fact, determined by the requirement that the forces on the ballooning thread and also those acting at the cap edge must be in equilibrium. Thus, if thread curves are calculated for a number of given top tensions (by the method outlined in the Appendix to this paper, or otherwise), the one appropriate to a given set of spinning conditions is that which satisfies the condition of equilibrium at the cap edge. In this way the effect of changing various technical features has been studied.

Spinning Conditions

The calculations refer to an idealized system in which the yarn is assumed to be in the form of a single thread of uniform circular cross section, perfectly flexible and inextensible. The air drag on the yarn is then reasonably assumed to vary according to the expression for an inclined wire, as discussed in the next section. It is further assumed that there are no frictional forces acting at the cap edge, which can be taken to imply that either the cap edge or the yarn or both are perfectly smooth. In view of the differences in the coefficient of friction from yarn to yarn and for different caps, and of the uncertainty of the correct value to take in any one case, this seems a reasonable assumption to make provided we do not wish to study the influence of cap-edge friction on the balloon. Values for the relevant coefficient of friction are usually about 0.2 or less, and thus the calculated results, and in particular the general conclusions, may be expected to give a good indication of the behavior to be expected in practice.

TABLE I

Height of balloon (h)	46 cm. (18.1 in.)
Radius of cap (R)	7.78 cm. (3 in.)
Radius of bobbin (b)	3.50 cm. (1.37 in.)
Spindle speed (N)	133.33 r.p.s. (8,000 r.p.m.)
Spinning speed (v)	833 cm./sec. (27.3 ft./sec.)
Speed of revolution of balloon ($\omega/2\pi$)	95.44 r.p.s. (5,726 r.p.m.)
Mass of yarn per unit length (m)	6.11×10^{-5} g./cm. (55 den.)
Diameter of hypothetical yarn	0.007 cm. (0.0028 in.)

The basic conditions of spinning are given in Table I, and the various graphs show the effects of varying different factors in turn.

Air Drag

In the previous paper the air drag on each element of yarn in the balloon was assumed to act horizontally. Here a better approximation is used to take account of the inclination of the thread to the vertical in some parts of the balloon. Measurements of air drag on inclined wires in an air stream, quoted in the *Handbook of Aeronautics* [2], indicate that for inclinations up to about 70° (which covers the range in which we are interested) the force on the wire is almost entirely normal to it, and is proportional to $\cos^2\theta$ in the region where the drag is proportional to (wind velocity)^2. Here θ is the angle between the normal to the wire and the direction of air flow. The main motion of an element ds of ballooning thread is horizontal and perpendicular to the radius to the element. The main component of drag is therefore normal to ds in the plane containing ds and ds_1, where ds_1 is the projection of ds on the meridian plane—*i.e.*, the plane containing the axis of the balloon and the radius to the element. In this case $\cos\theta = ds_1/ds$, and θ can conveniently be described as the "lean-back angle" of the yarn. This angle will vary along the yarn. If r denotes the radius to the element ds and ω is the angular velocity of the ballooning thread, the horizontal component of air drag on ds is

$$qr^2\omega^2 ds\cos^2\theta, \qquad (1)$$

where q is a constant for a given yarn and is proportional to yarn diameter if this is varied. The value for the basic diameter of 0.007 cm. deduced from data from the National Physical Laboratory [3] is $q = 0.58\times10^{-5}$ dynes sec.^{2} cm.$^{-5}$. There is also a radial component outwards and a downwards vertical component, but both of these are relatively small for the angles usually encountered in spinning, and so we have neglected them.

The equations of motion of an element of thread, with this expression for air drag included, and the method of solution are outlined in the Appendix.

Condition at the Cap Edge

The direction in which the ballooning thread approaches the cap edge is specified by the lean-back angle, θ_a, and by the inclination to the vertical of the plane containing ds and ds_1. Between the cap edge and the bobbin the thread is assumed to be straight and lies in a horizontal plane at an angle α to the radius to the point at which the thread leaves the cap edge. The angle α is given by

$$\sin\alpha = b/R, \qquad (2)$$

where b and R are the radii of bobbin and cap, respectively. If friction is eliminated, so that there is no change in tension as the thread crosses the cap edge, it is clear on resolving forces along the cap edge that for equilibrium we must have $\theta_a = \alpha$. By using the method described in the Appendix thread curves have been obtained for different values of the vertical component of tension (which is constant for a given case), and the curve appropriate to a given set of spinning conditions is that for which $\theta_a = \alpha$.

Calculated Results

In this paper "top tension" is the tension just below the top guide, and "bobbin tension" is the tension in the thread between the cap edge and the bobbin. As each factor is varied in turn, the others are assumed to keep the basic values listed in Table I unless they are related to the factor which is being varied. For example, a change in bobbin diameter necessarily involves a change in ω, the angular velocity of the ballooning thread, which must be considered.

Yarn Denier

An increase in yarn denier causes both bobbin tension and balloon diameter to increase, as shown in Figures 1 and 2. Bobbin tension is almost directly proportional to the denier. The corresponding curve for top tension is hardly distinguishable from that

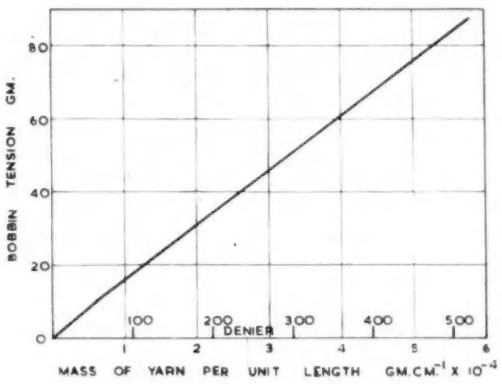

FIG. 1. *Effect of denier on bobbin tension.*

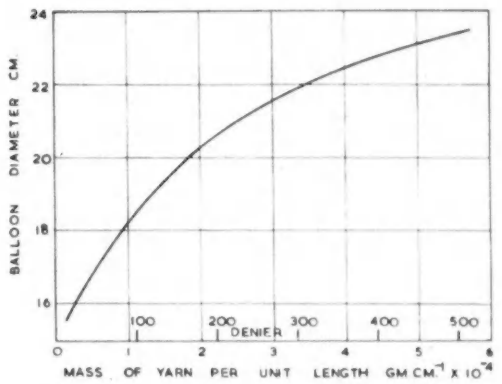

FIG. 2. *Effect of denier on balloon diameter.*

for bobbin tension and therefore is not shown here. The change in denier is assumed to be due to an increase in diameter of the yarn, the density remaining the same. It is worth noting that when 55/12 acetate yarn, to which our model filament is an approximation in equivalent cross-sectional area, was spun under these conditions, the tension observed by G. Curtis of Courtaulds Limited, Coventry, just above the top guide was 8.5 g. The calculated top tension, which is the tension just below the guide, was 10 g. The calculated results therefore give a reasonable indication of practical values, since a slight increase in tension is to be expected as the yarn passes through the guide.

Bobbin Speed

The equations of motion given in the Appendix in terms of nondimensional variables contain ω, the angular velocity of the balloon, only in the Coriolis terms. Since these are very small terms, we shall neglect any variation in them due to a change in ω. In this case ω is used only in converting the nondimensional tension, T_0, to grams by multiplying by $mh^2\omega^2$. Therefore, tension in grams must change as ω^2 to maintain T_0, and hence the thread curve, unchanged. The angular velocity of the balloon, ω, is related to the bobbin speed, N, by

$$\omega = 2\pi N - v/b, \qquad (3)$$

where v is the spinning speed and b is the bobbin radius, and so the dependence of bobbin tension on bobbin speed may be readily calculated. The relationship is shown graphically in Figure 3. Top tension is represented by almost the same curve. The balloon diameter and, in fact, the whole profile are unaltered by a change in bobbin speed.

Cap Diameter

In studying the effect of a change in cap diameter we have considered the bobbin diameter to be changed simultaneously in the same ratio. Figures 4 and 5 show that over the range considered bobbin tension and balloon diameter increase almost linearly as cap diameter is increased. Here again, the top tension is little different from the bobbin tension shown.

Bobbin Diameter

As the bobbin takes up yarn its diameter increases. The effect on bobbin tension is shown in Figure 6. This somewhat curiously shaped curve

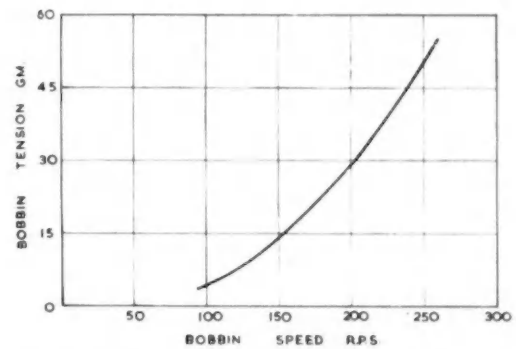

FIG. 3. *Effect of bobbin speed on bobbin tension.*

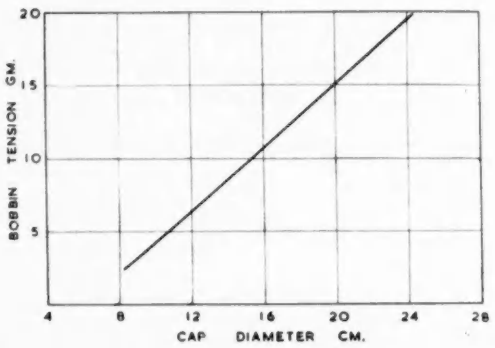

FIG. 4. *Effect of cap diameter on bobbin tension, the ratio of cap to bobbin diameters remaining constant.*

needs some explanation. First of all, an increase in bobbin diameter causes the balloon to rotate faster, according to expression (3), and we have already seen in Figure 3 that an increase in the angular velocity of the balloon (produced in that case by an increase in bobbin speed) causes the tension to increase. It is this increase in the speed of rotation of the balloon which causes the tension to increase in Figure 6 as the bobbin diameter changes from 4 to 7 cm. Beyond this the tension decreases as the bobbin diameter continues to increase, and this is the operating range used in practice, the diameter of the empty bobbin being 7 cm.

Furthermore, it is impossible to find from the curve of Figure 6 a tension corresponding to a bobbin diameter greater than about 9.5 cm. The explanation for this is to be found in Figure 7, where

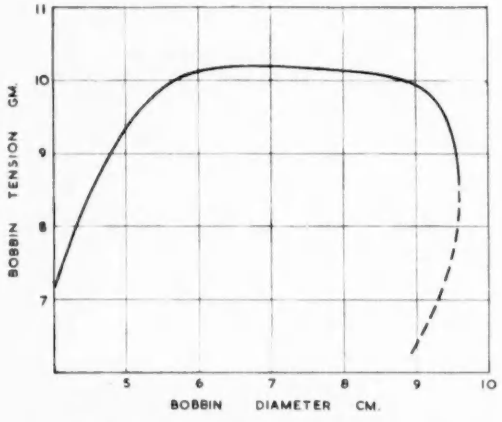

FIG. 6. *Effect of bobbin diameter on bobbin tension.*

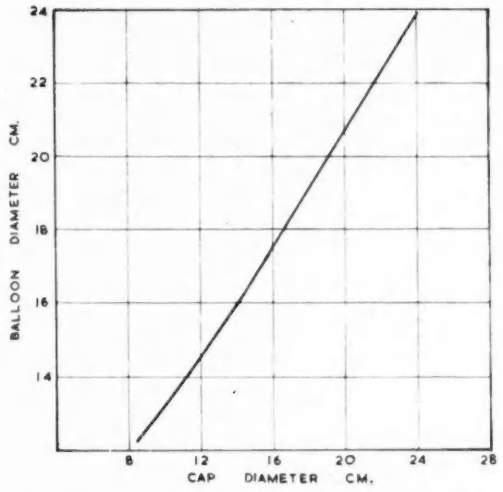

FIG. 5. *Effect of cap diameter on balloon diameter, the ratio of cap to bobbin diameters remaining constant.*

the nondimensional vertical component of tension, T_o, is plotted against sin θ_o for three different balloon heights, where θ_o is the lean-back angle at the cap edge. By referring to the Appendix it is seen that T_o is a parameter which is not specified by the dimensions of the spinning frame, the speeds, or the properties of the yarn. This is the parameter which is varied in order to find a value of θ_o such that the equilibrium condition at the cap edge, $\theta_o = \alpha$, is satisfied. Figure 7 shows that for any one height—*e.g.*, $h = 46$ cm.—as T_o is decreased, say from $T_o = 0.3$, sin θ_o increases and reaches a maximum value when $T_o = 0.12$ approximately. As T_o is decreased be-

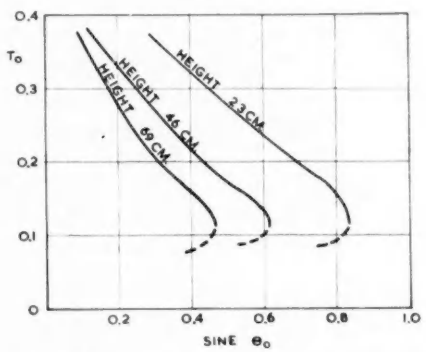

FIG. 7. *Effect of T_o on sin θ_o. T_o is a nondimensional vertical component of tension and θ_o is the lean-back angle at the cap edge.*

yond this value, sin θ_a decreases again. There is thus a certain lean-back angle which cannot be exceeded for any values of T_a. Remembering that sin $\alpha = b/R$, the value of T_a for any given bobbin radius is given by the ordinate of the appropriate curve of Figure 7 for which sin $\theta_a = b/R$. But if b/R exceeds the maximum value of sin θ_a, there is no value of T_a for which the equilibrium condition at the cap edge is satisfied. In other words, there is a maximum diameter of bobbin greater than which no free balloon can exist. For bobbin diameters greater than this in practice, the balloon collapses onto the cap and a new equilibrium condition is set up, with the balloon licking the side of the cap for part of its length. The existence of an upper limit to bobbin size beyond which no free balloons are possible has been deduced independently by Hannah [4] in a theoretical treatment of the cap spinning of wool. She also examined the new condition of equilibrium, in which the balloon rubs the cap, for the case of the cylindrical cap commonly used for wool spinning.

The existence of a maximum lean-back angle is accounted for to some extent by Figure 6 of the previous paper [1], which shows that there is a certain tension for which the balloon has a maximum diameter for given spinning conditions. This is roughly the same tension as that for which the limiting lean-back angle occurs, which is to be expected since the lean-back is caused primarily by air drag and this tends to decrease as the balloon gets smaller.

Figure 8 shows balloon profiles for two bobbin diameters—7 cm. and 9.6 cm., respectively. The balloon obtained with the larger bobbin shows slight "necking"—*i.e.*, a concavity is visible in the profile just above the cap edge. This necking may or may not cause the balloon to rub the side of the cap, depending on the shape of the cap. Thus, a balloon may rub the cap for two reasons: either because the tension is low enough to produce necking of a potentially free balloon or because the conditions are such —*e.g.*, too large a bobbin—that no free balloon can exist but only one supported on the side of the cap. The two cases are different in that it may be possible to prevent a necking balloon from rubbing the cap side by altering the shape of the cap, but a collapsed balloon can only exist in contact with the cap side.

Figure 7 suggests that any lean-back angle less than the maximum can be produced by two different values of T_a. Since the balloons corresponding to the lower alternative values of T_a seem unlikely to arise in normal practice, either because they are prevented by the presence of the cap or because they are unstable, we shall confine our attention to the higher values of T_a indicated by the solid lines on Figures 6, 7, and 9.

The diameter of a free balloon is not very dependent on bobbin radius, as is clear from Figure 8.

Balloon Height

Figure 9 shows how bobbin tension depends on balloon height. Here also there is a limiting height beyond which no free balloon is possible. It is clear from the curves for three different heights shown in Figure 7 that this must be so since the maximum sin θ_a which is possible theoretically is less the greater the balloon height. Thus, for given bobbin and cap

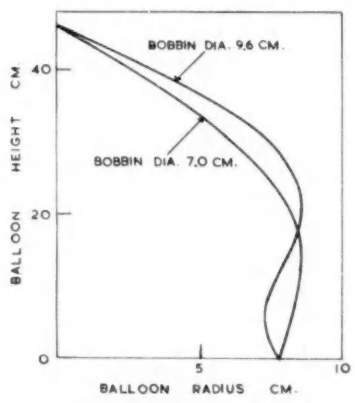

FIG. 8. *Balloon profiles for two bobbin diameters.*

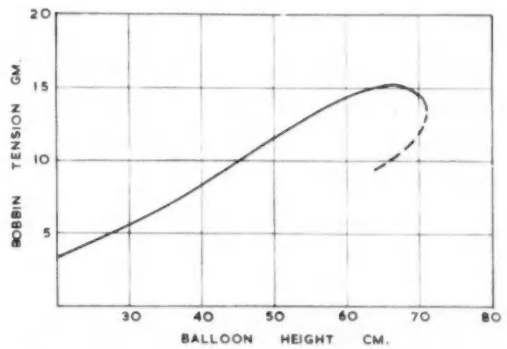

FIG. 9. *Effect of balloon height on bobbin tension.*

radii, for which $\sin \theta_o = 0.62$, for example, curves of the type shown in Figure 7 for balloon height less than 46 cm. intersect the ordinate at $\sin \theta_o = 0.62$ at two points, and, as stated above, we take the higher value of T_o to be the one obtained in practice; the curves for heights exceeding 46 cm. do not intersect this ordinate at all, and no free balloons are possible. The curve of Figure 7 for a height of 46 cm. touches the ordinate at $\sin \theta_o = 0.62$ and this would be the limiting height for this particular cap and bobbin. It is clear that the limiting balloon height decreases as the bobbin radius increases, and, similarly, the limiting bobbin radius discussed above decreases as the balloon height is increased.

Figure 10 shows balloon profiles for three different heights. Two points are to be noted. First, the highest balloon shows signs of necking, although the others do not. Second, a change in balloon height has little effect on the diameter of the balloon. This cannot be considered to be true in general, for Figure 6 of the previous paper [1] shows that there is only a limited range of tension over which the balloon diameter is independent of tension.

The calculated results of this paper are in general agreement with those obtained by Hannah [4] using a different method of calculation based on simpler assumptions. Her calculations refer to the cap spinning of wool. She assumed the air drag on an element of ballooning yarn to act horizontally, and, also, in the nomenclature of the Appendix, $ds = dz$ everywhere. Her final solution is therefore comparable with the first approximation in the iterative method outlined in the Appendix.

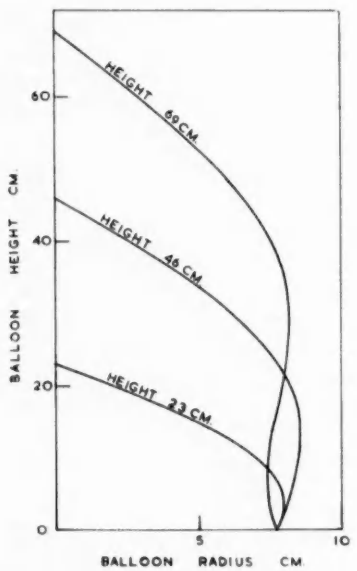

FIG. 10. *Balloon profiles for three balloon heights.*

Summary

The influence of balloon height, cap and bobbin size, bobbin speed, and yarn denier on balloon size and thread tension was investigated theoretically. Balloon diameter and bobbin tension both increase with increasing denier, cap diameter, and bobbin speed. There is a maximum size of bobbin greater than which no free balloon exists but only one which rubs the side of the cap. Similarly, for a given bobbin all balloons of more than a certain height rub the cap side. Over the range considered, bobbin size and balloon height have little effect on balloon diameter.

Appendix

With reference to axes OX, OY, and OZ rotating about OZ with the constant angular velocity, ω, of the ballooning thread, the equations of motion embodying the assumptions stated in the main text are

$$\frac{d}{ds}\left(T_z \frac{dx}{dz}\right) + \frac{fy}{r}\cos^3\theta + 2mv\omega\frac{dy}{ds} + m\omega^2 x = 0 \quad (4)$$

and

$$\frac{d}{ds}\left(T_z \frac{dy}{dz}\right) - \frac{fx}{r}\cos^3\theta - 2mv\omega\frac{dx}{ds} + m\omega^2 y = 0. \quad (5)$$

Here s is the distance along the thread and T_z is the vertical component of a modified thread tension, $T - mv^2$, where T is the true tension in grams (for other nomenclature see Table I). If gravity and the small vertical component of air drag are neglected, T_z is constant. Writing

$$T_o = T_z/mh^2\omega^2, \quad \xi = x/R, \quad \eta = y/R, \quad \zeta = z/h,$$
$$\sigma = s/h, \quad \rho = r/R, \quad (6)$$

and

$$f = qr^2\omega^2, \quad (7)$$

equations (4) and (5) become

$$\frac{d}{d\sigma}\left(T_o \frac{d\xi}{d\zeta}\right) + \frac{qR}{m}\rho\eta\cos^3\theta + \frac{2v}{h\omega}\frac{d\eta}{d\sigma} + \xi = 0 \quad (8)$$

and

$$\frac{d}{d\sigma}\left(T_o \frac{d\eta}{d\zeta}\right) - \frac{qR}{m}\rho\xi\cos^3\theta - \frac{2v}{h\omega}\frac{d\xi}{d\sigma} + \eta = 0. \quad (9)$$

By using a differential analyzer [5], solutions of equations (8) and (9) have been obtained for different values of T_o, satisfying the conditions

$$\xi = \eta = 0, \quad \zeta = 0, \tag{10}$$

$$\rho = 1, \quad \zeta = 1. \tag{11}$$

The differential analyzer available in this Laboratory has not enough integrating units to deal with equations (8) and (9) directly and therefore the following method of successive approximations was used. For the first approxiation we assume $d\sigma = d\zeta$ and $\theta = 0$ everywhere, and a solution of (8) and (9), appropriately simplified, is then obtained by using the differential analyzer. From this solution σ and $\cos^3 \theta$ are evaluated as functions of ζ, and are then fed into the analyzer in order to obtain an approximate solution of the full equations (8) and (9). This procedure yields second approximations to σ and $\cos^3 \theta$ as functions of ζ, which can be fed into the machine to obtain a further approximation to the solution, and so on. Usually the third and fourth approximations agree sufficiently closely to be taken as the required solution for present purposes.

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Relationship of Fineness in Wool Top, Noil, Card Sliver, and Grease Wool*

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Introduction

There are many physical properties and characteristics which give wool its usefulness as a textile fiber. Of these, fineness, or fiber diameter, is considered the most important dimensional characteristic in establishing the manufacturing utility and commercial value of wool. For this reason, fiber fineness has formed the basis for the standards and grades which have been developed for wool.

In 1926, the U.S.D.A. developed grades for matchings of grease wool based on diameter of fiber. These grades, twelve in number, were developed and officially promulgated in order to provide a common basis of understanding among growers, buyers, and others interested in the marketing, trading, and processing of wool. The specifications for the grades that were developed, however, were entirely on a visual basis, which meant that the grade for any particular lot of grease wool matchings had to be determined by comparison with the official grades.

Official standards for grades 80s to 50s, inclusive, of wool top, a product which results from the scouring, carding, and combing of the grease wool, were established on a quantitative measurement basis some years ago. It appears logical, therefore, that corresponding grease wool grades also should be established on a quantitative basis. However, in order to develop specifications for fiber diameter and distribution in grades of grease wool in such a way

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that they will tie in with the specifications for the corresponding grades of wool top, it is necessary to study the dimensional changes which grease wools undergo in processing. In other words, data must be developed to show the changes that take place in fiber diameter and distribution in the grease wool when it has been made into wool top, as top generally is the final stage of processing wool prior to making yarn. Moreover, since top ordinarily represents the form of the product in which fineness determinations are made by industry and the trade, it appears logical to use the quantitative specifications for top as a basis for the specifications to be developed for grease wool.

Consequently, the present study had for its major objectives: (*1*) the determination of the relationships in fiber fineness and distribution of grease wool and wool top resulting from the processing; and (*2*) the development of adequate sampling procedures and appropriate analytical methods. Although the findings reported in this publication are not conclusive, the results are highly significant in terms of methodology and general indications.

The preliminary study covered twenty-four lots of wool matchings, grades 70s, 64s, 62s, and 60s. These grades represent approximately 70% of the domestic shorn wool clip, and, for the most part, such wools are used in the worsted system of manufacture. Data covering the quantitative relationships in fiber fineness and distribution between the other grades of grease wool matchings and resultant top are being obtained.

Experimental Procedure

Lots of grease wool in the process of being combed were sampled, and samples were also drawn from the card sliver, top, and noils during the processing operations. Samples of card sliver were drawn for fineness measurements, as such a measurement was considered to be an excellent check on the sampling adequacy of the grease wool. Samples of noils were drawn in order to determine fineness, as such, and also in order to determine the effect of the removal of the noils on the relationship between fineness and distribution of grease wool and resultant top.

Of the twenty-four lots studied, two were grade 70s, nine were 64s, ten were 62s, and three were 60s.

Grease Wool

Two methods were used in obtaining samples of the grease wool for fineness testing. One method consisted of drawing hand-samples of approximately 3 lbs. each, at random, from the pile after matchings were ready for scouring or after the blends were made. The second method involved the use of scoured subsamples of 3-in. core samples which had been drawn from the grease wool for shrinkage determination.

Each hand-sample was spread out on a table, and twenty-five pieces were selected at random. Locks weighing approximately 5 g. each were drawn from each of the twenty-five pieces, and these locks were blended into a composite sample. The composite grease wool sample then was hand-dusted, blended, and scoured in an aqueous solution of soda ash and detergent. The scoured samples were homogenized by running the dried wool through a small carding machine. The sliver from the first carding was mixed by hand and run through the carding machine a second time.

Each 3-in. scoured core sample was packed tightly into a cylinder 3 in. in diameter and cored

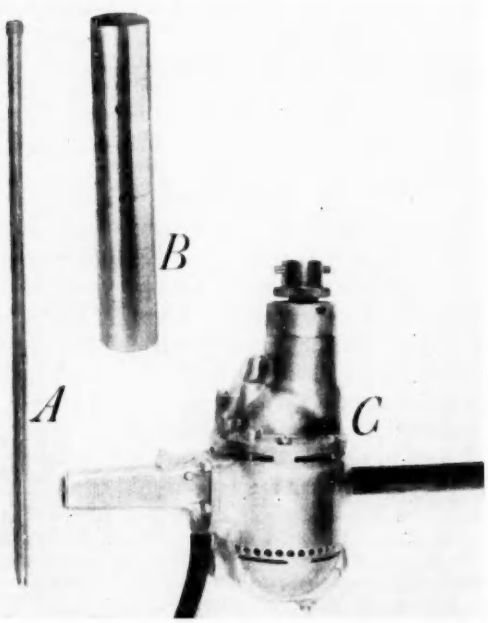

FIG. 1. *Equipment used in subsampling scoured cores: A—½-in. tube; B—3-in. cylinder; C—electric drill.*

lengthwise through the cylinder with a ½-in. rotary core. Several of these small cores were taken in this manner until approximately 7 g. were obtained. The equipment used in the subsampling is shown in Figure 1.

Top and Card Sliver

Samples of a few feet of top and of card sliver were drawn at various stages during the processing of the grease wool lot which had been sampled. These samples were then reduced to workable size for fineness measurements by clipping small sections at random from each of the different pieces of top and from each of the pieces of card sliver. These sections for each product, in turn, were combined into a composite sample.

Noil

A small quantity of noils was collected at the same time that the top samples and card sliver samples were drawn. From the bulk of each noil sample, small clumps were drawn at random until about 7 g. had been obtained.

Comparison of the Grease Wool Sampling Methods

The major objective involved in this phase of the work was to determine the adequacy and the best method of sampling grease wool in making fineness analyses. Since card sliver represents grease wool which has been scoured and homogenized, without any appreciable loss of fibers, and since card sliver does not present any material difficulty in sampling, the adequacy of any sampling of grease wool generally can be determined by comparing the respective average fineness results and standard deviations. Table I shows the results of such comparison for each lot tested.

Very little difference was found between the average fineness of card sliver and grease wool for the

TABLE I. RELATIONSHIP BETWEEN AVERAGE FIBER DIAMETER AND STANDARD DEVIATION IN GREASE WOOL AND CARD SLIVER, BY GRADES OF WOOL

Grade	Grease wool		Card sliver		Difference in average diameter* (μ)
	Average diameter (μ)	Standard deviation (μ)	Average diameter (μ)	Standard deviation (μ)	
70s	20.51	3.1	20.97	3.6	+0.46
70s	20.98	3.8	20.37	3.8	
Average	20.7	3.5	20.70	3.7	0.54
64s	21.61	4.8	20.48	4.6	−1.13
64s	22.03	3.6	22.25	4.2	+0.22
64s	22.84	3.6	22.27	4.3	−0.57
64s	22.06	4.3	22.07	5.2	+0.01
64s	20.05	3.5	20.65	4.2	+0.60
64s	21.20	4.1	20.92	3.9	−0.28
64s	19.70	3.8	20.38	3.8	+0.68
64s	21.38	4.9	21.50	4.6	+0.12
64s	23.62	5.4	21.95	5.0	−1.67
Average	21.6	4.2	21.40	4.4	0.59
62s	22.46	5.0	22.24	4.7	−0.22
62s	22.39	4.9	22.89	4.8	+0.50
62s	24.09	4.8	23.17	5.4	−0.92
62s	24.16	5.0	23.50	4.6	−0.66
62s	23.74	6.0	23.70	6.0	−0.04
62s	21.97	4.8	22.15	4.8	+0.18
62s	21.88	5.0	22.48	4.5	+0.60
62s	23.03	4.9	23.05	5.3	+0.02
62s	23.28	5.4	23.70	5.5	+0.42
62s	24.02	5.0	23.35	5.3	−0.67
Average	23.1	5.1	23.00	5.1	0.42
60s	24.53	6.3	23.98	5.5	−0.55
60s	25.98	6.3	24.84	5.6	+1.14
60s	23.85	5.3	23.88	5.0	−0.03
Average	24.8	6.0	24.20	5.4	0.57

* Card sliver was used as the base in determining differences.

grades 64s and 62s. This was true also for fiber variability, as expressed by the standard deviation.

As shown in Table I, there appears to be no definite pattern in the differences between the average diameter of grease wool and card sliver. The grease wool was coarser than the card sliver in twelve of the twenty-four lots, and in the remaining twelve lots the card sliver was coarser. The mean difference between the grease wool and card sliver for the 70s was 0.54 μ, and for the 64s, 62s, and 60s it was 0.59 μ, 0.42 μ, and 0.57 μ, respectively. Based on the average fineness for the lots of each grade tested, there was no practical difference between the grease wool and the card sliver for the 70s, 64s, and 62s.

A comparison of the average fineness of card sliver and the average fineness of grease wool according to the sampling method of the grease wool is shown in Figure 2. As shown in this chart, the difference in average fineness between card sliver and grease wool samples drawn by coring was smaller than that between card sliver and grease wool samples drawn by hand. In the 64s, 62s, and 60s grades, there was only 0.1 μ difference between the average fineness of the card sliver and the average of the grease wool represented by core samples.

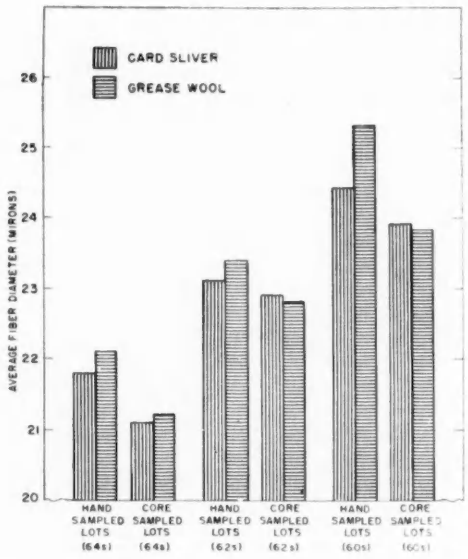

FIG. 2. *Comparison of the average fineness of card sliver and the average fineness of grease wool, according to the sampling method of the grease wool.*

The difference between the average fineness of the card sliver and the grease wool hand-samples, on the

TABLE II. TYPE OF COMBING, AVERAGE FIBER DIAMETER, STANDARD DEVIATION, AND COEFFICIENT OF VARIATION FOR TOP, NOIL, CARD SLIVER, AND GREASE WOOL FOR LOTS WITHIN THE OFFICIAL GRADE LIMITS FOR 70S AND 64S TOP

		Top			Noil			Card sliver			Grease wool		
Grade	Type of combing	Average diameter (μ)	Standard deviation (μ)	Coefficient of variation (%)	Average diameter (μ)	Standard deviation (μ)	Coefficient of variation (%)	Average diameter (μ)	Standard deviation (μ)	Coefficient of variation (%)	Average diameter (μ)	Standard deviation (μ)	Coefficient of variation (%)
70s	French	20.85	4.09	19.62	18.78	3.75	19.97	20.97	3.58	17.07	20.51	3.10	15.11
70s	Noble	20.85	3.83	18.37	20.01	3.78	18.80	20.37	3.77	18.51	20.98	3.81	18.16
Average		20.80	4.00	19.00	19.40	3.80	19.40	20.70	3.70	17.80	20.70	3.50	16.60
64s	French	21.28	4.55	21.38	19.90	3.53	17.74	20.48	4.55	22.22	21.61	4.80	22.21
64s	Noble	22.00	3.97	18.05	19.88	3.93	19.77	22.25	4.20	18.88	22.03	3.57	16.21
64s	French	22.06	4.34	19.67	20.77	4.65	22.39	22.27	4.31	19.35	22.84	3.62	15.82
64s	Noble	22.27	5.18	23.26	20.07	5.00	23.96	22.07	5.24	23.74	22.06	4.30	19.46
Average		21.90	4.50	20.60	20.40	4.30	21.00	21.80	4.60	21.00	22.10	4.10	18.40
64s*	French	21.28	4.20	19.74	19.18	4.03	21.01	20.65	4.18	20.24	20.05	3.52	17.56
64s*	Noble	21.78	4.02	18.46	19.80	3.93	19.85	20.92	3.88	18.55	21.20	4.15	19.58
64s*	Noble	21.80	4.70	21.56	19.18	3.85	20.07	20.38	3.82	18.74	19.70	3.80	19.29
64s*	French	22.30	4.90	21.97	19.15	4.25	21.85	21.50	4.62	21.49	21.38	4.85	22.68
64s*	Noble	22.42	4.98	22.21	20.78	4.85	23.34	21.95	4.95	22.55	23.62	5.42	22.95
Average		21.90	4.60	20.80	19.60	4.20	21.20	21.10	4.30	20.30	21.20	4.30	20.40
Average of all 64s		21.9	4.5	20.7	19.9	4.2	21.1	21.4	4.4	20.6	21.6	4.2	19.5

* Grease wool cored for shrinkage; fineness of scoured core-samples representing the grease wool.

other hand, ranged from 0.3μ for the 64s grade to 0.9μ for the 60s.

It is often asserted that the average diameter of wool top should be greater than the average diameter of the grease wool from which it came. In comparing results on the lots involved in this study, it was found that the grease wool measured coarser than the top in eight of the thirteen lots hand-sampled, but in only two of the eleven lots core-sampled.

Discussion of Results of the Study

The measurement results for most lots in this study were in general agreement with the concept that the fineness of grease wool is altered when processed into wool top. That is, some of the short, fine fibers are removed in the combing operations, which results in the top being slightly coarser than the grease wool from which it was made. However, potential sampling and measurement errors would tend to obscure the precise differences between the

TABLE III. TYPE OF COMBING, AVERAGE FIBER DIAMETER, STANDARD DEVIATION, AND COEFFICIENT OF VARIATION FOR TOP, NOIL, CARD SLIVER, AND GREASE WOOL FOR LOTS WITHIN THE OFFICIAL GRADE LIMITS FOR 62S AND 60S TOP

		Top			Noil			Card sliver			Grease wool		
Grade	Type of combing	Average diameter (μ)	Standard deviation (μ)	Coefficient of variation (%)	Average diameter (μ)	Standard deviation (μ)	Coefficient of variation (%)	Average diameter (μ)	Standard deviation (μ)	Coefficient of variation (%)	Average diameter (μ)	Standard deviation (μ)	Coefficient of variation (%)
62s	French	22.61	5.38	23.79	21.29	4.99	23.44	22.24	4.71	21.18	22.46	5.00	22.26
62s	French	22.82	4.98	21.82	20.61	4.79	23.24	22.89	4.81	21.48	22.39	4.90	21.88
62s	Noble	23.38	5.08	21.73	20.66	4.95	23.96	23.17	5.39	23.26	24.09	4.85	20.13
62s	Noble	23.87	4.49	18.81	21.78	5.02	23.05	23.50	4.64	19.74	24.16	5.02	20.78
62s	Noble	23.93	5.70	23.82	21.59	5.37	24.87	23.70	5.96	25.15	23.74	5.95	25.06
Average		23.30	5.10	22.00	21.20	5.00	23.70	23.10	5.10	22.20	23.40	5.10	22.00
62s*	French	22.72	5.15	22.67	20.75	4.58	22.07	22.15	4.85	21.90	21.97	4.84	22.03
62s*	French	23.65	5.20	21.99	21.40	4.62	21.59	22.48	4.50	20.02	21.88	5.05	23.08
62s*	Noble	23.81	5.47	22.96	21.33	4.93	23.11	23.05	5.27	22.86	23.03	4.93	21.41
62s*	French	23.85	5.72	23.98	21.00	5.15	24.52	23.70	5.50	23.21	23.28	5.38	23.11
62s*	Noble	23.95	5.25	21.92	20.85	4.85	23.26	23.35	5.30	22.70	24.02	5.02	20.90
Average		23.60	5.40	22.70	21.10	4.80	22.90	22.90	5.10	22.10	22.80	5.00	22.10
Average of all 62s		23.5	5.2	22.4	21.1	4.9	23.3	23.0	5.1	22.2	23.1	5.1	22.1
60s	French	24.04	5.66	23.54	20.81	4.91	23.59	23.98	5.51	22.98	24.53	6.34	25.85
60s	Noble	24.78	5.59	22.56	22.84	5.53	24.21	24.84	5.58	22.46	25.98	6.26	24.10
Average		24.40	5.60	23.10	21.80	5.20	23.90	24.40	5.60	22.70	25.30	6.30	25.00
60s*	Noble	24.50	5.52	22.53	21.62	5.48	25.35	23.88	5.02	21.02	23.85	5.32	23.14
Average of all 60s		24.4	5.6	22.9	21.8	5.3	24.4	24.2	5.4	22.2	24.8	6.0	24.4

* Grease wool cored for shrinkage; fineness of scoured core-samples representing the grease wool.

TABLE IV. COMPARISON OF AVERAGE FIBER DIAMETER OF WOOL TOP, NOIL, CARD SLIVER AND GREASE WOOL, BY GRADE

		Top	Noil		Card sliver		Grease wool	
Grade	Lots (no.)	Average diameter (μ)	Average diameter (μ)	Difference between top and noil* (μ)	Average diameter (μ)	Difference between top and card sliver (μ)	Average diameter (μ)	Difference between top and grease wool (μ)
70s	2	20.8	19.4	+1.4	20.7	+0.1	20.7	+0.1
64s	9	21.9	19.9	+2.0	21.4	+0.5	21.6	+0.3
62s	10	23.5	21.1	+2.4	23.0	+0.5	23.1	+0.4
60s	3	24.4	21.8	+2.6	24.2	+0.2	24.8	−0.4

* The plus sign signifies that the average diameter of top is coarser than the average diameter with which it is being compared, and the minus sign signifies the reverse.

fineness of grease wool, card sliver, and top, especially if the differences are as small as those applying to the lots of 70s and 64s tested in this experiment. Consequently, in order to compensate for any sampling and measurement errors involved, a greater number of tests will be necessary in order to disclose more precisely the magnitude of the changes which take place in fineness and distribution in the various grades and in different wools as a result of processing operations.

The fineness measurements for the lots classified as 70s and 64s are shown in Table II, and those for lots classified as 62s and 60s are shown in Table III.

An analysis of the data presented in Tables II, III, and IV shows that the average fineness of the top, when considered grade by grade, is coarser than the average fineness of the noil, the card sliver, and the grease wool, with the exception of grade 60s. For this grade, the average fineness of the grease wool was 0.4μ coarser than the top and 0.6μ coarser than the card sliver, indicating the possibility of a small sampling error.

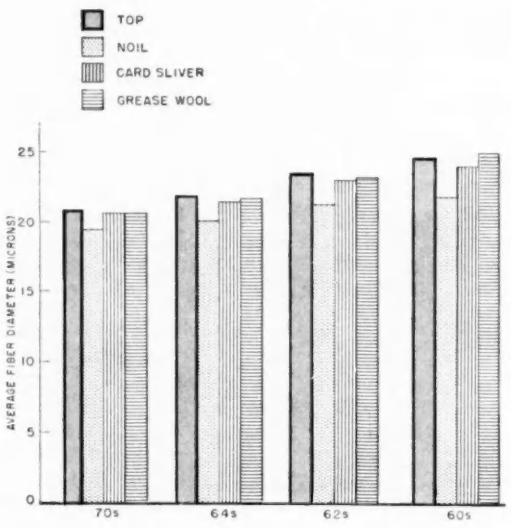

FIG. 3. *Comparison of average fiber diameter of wool top, noil, card sliver, and grease wool, according to the grade of wool.*

TABLE V. FIBER DISTRIBUTION OF TOP, GREASE WOOL, CARD SLIVER, AND NOIL FOR 5 LOTS OF THE 64S GRADE

Lot No.	Sample	Average fiber diameter (μ)	Standard deviation (μ)	Coefficient of variation (%)	Fiber distribution 10.0–20.0μ (%)	20.1–30.0μ (%)	30.1–40.0μ (%)	40.1–50.0μ (%)	50.1–60.0μ (%)
1	top	21.28	4.20	19.74	42.83	53.51	3.66	—	—
	grease wool	20.05	3.52	17.56	54.00	45.00	1.00	—	—
	card sliver	20.65	4.18	20.24	46.75	51.00	2.00	0.25	—
	noil	19.18	4.03	21.01	63.50	34.25	2.25	—	—
2	top	21.78	4.02	18.46	34.67	62.97	2.49	0.17	—
	grease wool	21.20	4.15	19.58	42.49	55.67	1.50	0.34	—
	card sliver	20.92	3.88	18.55	46.82	51.51	1.67	—	—
	noil	19.80	3.93	19.85	56.25	42.50	1.25	—	—
3	top	21.80	4.70	21.56	34.50	61.25	3.75	0.50	—
	grease wool	19.70	3.80	19.29	58.25	40.75	1.00	—	—
	card sliver	20.38	3.82	18.74	49.75	49.00	1.25	—	—
	noil	19.18	3.85	20.07	62.75	36.50	0.75	—	—
4	top	22.30	4.90	21.97	34.34	58.16	7.17	0.33	—
	grease wool	21.38	4.85	22.68	43.16	50.50	6.00	0.34	—
	card sliver	21.50	4.62	21.49	42.33	52.66	5.01	—	—
	noil	19.15	4.25	21.85	58.00	40.50	1.50	—	—
5	top	22.42	4.98	22.21	33.99	59.00	6.67	0.34	—
	grease wool	23.62	5.42	22.95	24.66	63.83	10.84	0.50	0.17
	card sliver	21.95	4.95	22.55	39.00	54.83	5.50	0.67	—
	noil	20.78	4.85	23.34	48.84	46.83	4.16	0.17	—
Weighted average of 5 lots	top	21.9	4.6	20.8	36.18	58.75	4.82	0.25	—
	grease wool	21.2	4.3	20.4	42.73	52.42	4.55	0.27	0.03
	card sliver	21.1	4.3	20.3	44.42	52.07	3.32	0.19	—
	noil	19.6	4.2	21.2	57.13	40.71	2.12	0.04	—

The data show that the magnitude of the difference between average fineness of top and noil increased as the coarseness of the top increased. These differences ranged from 1.4μ for the 70s to 2.6μ for the 60s.

The spread between the average fineness of the top and card sliver ranged from 0.1μ for the 70s to 0.5μ for the 64s and 62s. Between top and grease wool, the range was from 0.1μ for the 70s to 0.4μ for the 64s and 62s. The spread between the fineness of top and noil varied from 1.4μ for the 70s to 2.6μ for the 60s wool.

Table IV and Figure 3 show a summary of average fiber diameter of wool top, noil, card sliver, and grease wool, by grades. Differences between these averages also are shown.

An analysis of the results for individual lots, as shown in Tables II and III, indicates that average fiber diameter of the card sliver for five lots was coarser than that of the resultant top. However, the greatest difference in average diameter was 0.25μ and the average only 0.14μ; hence sampling and measurement errors probably were responsible.

The fineness relationships between top, noil, card sliver, and grease wool found in this preliminary study are in general agreement with the fineness relationship between top, card sliver, and grease wool of the four master wools of the international Wool Research Project being conducted at Textile Research Institute and Forstmann Woolen Company.*

Fiber Distribution and Uniformity

Fiber fineness distribution data were analyzed for five lots of the 64s, five lots of the 62s, and one lot of the 60s. The analysis covered grease wool, card sliver, top, and noils. The results are shown in Tables V, VI, and VII. The average fiber diameter, standard deviation, and coefficient of variation are given for comparative purposes. The fiber distributions are shown in class intervals of 10μ.

When the fiber distributions of top, grease wool, and card sliver were compared, it was noted that, for most lots, a smaller percentage of fibers was

* von Bergen, W., What's New in Wool Research, *The National Wool Grower*, Jan. 1952.

TABLE VI. FIBER DISTRIBUTION OF TOP, GREASE WOOL, CARD SLIVER, AND NOIL FOR 5 LOTS OF THE 62S GRADE

Lot No.	Sample	Average fiber diameter (μ)	Standard deviation (μ)	Coefficient of variation (%)	Fiber distribution 10.0–20.0μ (%)	20.1–30.0μ (%)	30.1–40.0μ (%)	40.1–50.0μ (%)	50.1–60.0μ (%)
1	top	22.72	5.15	22.67	32.67	57.66	8.83	0.84	—
	grease wool	21.47	4.84	22.03	37.58	56.68	5.58	0.16	—
	card sliver	22.15	4.85	21.90	34.50	58.66	6.33	0.51	—
	noil	20.75	4.58	22.07	49.00	48.25	2.00	0.75	—
2	top	23.65	5.20	21.99	25.67	62.99	10.84	0.50	—
	grease wool	21.88	5.05	23.08	38.99	54.19	6.50	0.64	—
	card sliver	22.48	4.50	20.02	30.25	60.66	8.59	0.50	—
	noil	21.40	4.62	21.59	40.00	55.66	4.00	0.34	—
3	top	23.81	5.47	22.96	24.83	62.59	11.50	1.00	0.08
	grease wool	23.03	4.93	21.41	27.91	62.48	8.97	0.64	—
	card sliver	23.05	5.27	22.86	30.25	60.66	8.59	0.50	—
	noil	21.33	4.93	23.11	46.16	48.17	5.50	0.17	—
4	top	23.85	5.72	23.98	26.50	60.00	12.33	1.17	—
	grease wool	23.28	5.38	23.11	27.84	62.33	8.83	1.00	—
	card sliver	23.70	5.50	23.21	25.66	62.67	10.83	0.84	—
	noil	21.00	5.15	24.52	47.50	48.16	3.83	0.34	0.17
5	top	23.95	5.25	21.92	22.33	65.34	11.83	0.50	—
	grease wool	24.02	5.02	20.90	21.75	66.01	11.63	0.61	—
	card sliver	23.35	5.30	22.70	29.66	59.51	10.33	0.50	—
	noil	20.85	4.85	23.26	47.66	48.17	3.83	0.34	—
Weighted average of 5 lots	top	23.6	5.4	22.7	26.13	61.87	11.13	0.84	0.03
	grease wool	22.8	5.0	22.1	29.82	61.16	8.48	0.54	—
	card sliver	22.9	5.1	22.1	30.28	60.86	8.38	0.48	—
	noil	21.1	4.8	22.9	45.86	49.78	3.96	0.36	0.04

found in the 10–20μ group for top than was the case either for the grease wool or the card sliver. For most lots, also, the top showed a larger percentage of fibers in the 20.1–30.0μ, the 30.1–40.0μ, and 40.1–50.0μ groups than was the case with grease wool or card sliver. This difference can be expected since noils, which include a large percentage of the finest fibers, have been removed.

The fibers within the 10–20μ groups in the distribution of card sliver for the grades 64s, 62s, and 60s averaged 44.42%, 30.28%, and 21.84%, respectively, as compared with 36.18%, 26.13%, and 20.69% for the corresponding grades of top.

In the 20.1–30.0μ group, the top comprised 58.75% of the fibers for the 64s, as compared with 52.07% for the card sliver. For this group in the 62s, the top comprised 61.87% and the card sliver 60.86% of the fibers. The corresponding figures in this group for the 60s were 64.50% for the top and 67.51% for the card sliver.

The 64s, 62s, and 60s grades of top comprised 4.82%, 11.13%, and 13.80% of the fibers in the 30.1–40.0μ group, respectively, as compared with 3.32%, 8.38%, and 9.99% for the corresponding card sliver distributions.

The fiber distribution for 64s top showed 0.25% in the 40.1–50μ group, as compared with 0.19% for the card sliver. For 62s, the corresponding figures were 0.84% and 0.48%. For 60s, the top showed 1.0%, as compared with 0.66% for the card sliver.

The results of the tests on noil showed that the greatest percentage of fibers removed during combing operations were the finer ones. However, there also are fibers in the noil covering the entire range in fiber distribution found in the top.

An analysis of the data in Tables II and III indicated that the standard deviation and coefficient of variation for fiber distribution in top tended to be slightly higher than those of the card sliver and grease wool. However, as with average fiber diameter, some lots of card sliver and grease wool showed a greater standard deviation and a higher coefficient of variation than their corresponding tops. In most cases, the differences found were small and probably resulted from minor sampling and testing errors.

Calculated maximum standard deviations for grades of top have been suggested by Wadley, Pohle, and Mueller.* The suggestion was that lots showing higher values of standard deviation than those shown in Table VIII would be considered too high in dispersion to meet official specifications for grades of top.

All the samples of top, card sliver, and grease wool tested in the present study showed standard deviations within the maximum indicated for the corresponding grades.

Conclusions

The following tentative conclusions were drawn from the study:

1. The average fineness of top apparently is coarser than the average fineness of noil, card sliver, and grease wool.

2. The spread between the average fineness of the top and the average fineness of noil, card sliver, and grease wool increases slightly with the coarseness of the wool.

3. There is no significant difference between the average fineness of card sliver and grease wool for the lots tested.

* Wadley, F. M., Pohle, E. M., and Mueller, W. A., Easier Grade Determination by Measurement in Wool Top, TEXTILE RESEARCH JOURNAL **19**, 278 (May 1949).

TABLE VII. FIBER DISTRIBUTION OF TOP, GREASE WOOL, CARD SLIVER, AND NOIL FOR 1 LOT OF 60S GRADE

Lot No.	Sample	Average fiber diameter (μ)	Standard deviation (μ)	Coefficient of variation (%)	Fiber distribution 10.0–20.0μ (%)	20.1–30.0μ (%)	30.1–40.0μ (%)	40.1–50.0μ (%)	50.1–60.0μ (%)
1	top	24.50	5.52	22.53	20.69	64.50	13.80	1.00	0.10
	grease wool	23.85	5.32	23.14	26.10	61.80	11.70	0.40	—
	card sliver	23.88	5.02	21.02	21.84	67.51	9.99	0.66	—
	noil	21.62	5.48	25.35	43.00	48.38	8.12	0.50	—

TABLE VIII. SUGGESTED MAXIMUM STANDARD DEVIATIONS FOR GRADES OF TOP

Standard deviation (μ)	80s	70s	64s	62s	60s	58s	56s	50s	48s	46s	44s	40s	36s
Maximum	4.4	5.0	5.5	6.0	6.4	6.9	7.4	8.1	8.5	8.8	9.2	9.7	10.2

4. The difference found in average diameter between the card sliver and the grease wool was smaller when cores rather than hand-samples were used.

5. For the lots tested, there was a general tendency for the standard deviation and coefficient of variation of top to be slightly higher than those for corresponding card sliver and grease wool.

6. Since grades and types of grease wool differ in their inherent fiber characteristics, a large number of tests will be necessary in order to determine the average magnitude of the changes that take place in fiber fineness and variability during processing into top. The results obtained in this preliminary study indicate that the number of tests involved was insufficient to compensate for normal sampling and testing errors.

7. Since the quantitative relationship in the fineness of grease wool to wool top is needed as a basis for developing numerical specifications for grades of grease wool, sufficient additional tests should be made to determine the average relationship for preparing the standards for grease wool.

Acknowledgment

Special credit is due the manufacturers, top makers, wool growers, and others who furnished wool and so willingly cooperated in the collection of samples used in the study.

(Manuscript received April 13, 1953.)

Book Reviews

Textile Chemicals and Auxiliaries. Edited by Henry C. Speel. New York, Reinhold Publishing Corp., 1952. 493 pages. Price, $10.00.

(Reviewed by Hillary Robinette, Jr., Chemical Consultant, Ardmore, Pa.)

The assembling and organizing of the information related to the nature and wet processing, dyeing, printing, and finishing of textiles have been ably accomplished by Editor Speel. *Textile Chemicals and Auxiliaries* adequately fills the need of supplying practical information about all of the phases of textile processing. It contains twenty-three chapters prepared by various well-known specialists in the textile and textile chemical industries.

The book is divided into two parts. The first part, containing seven chapters, deals with the physical and chemical aspects of fibers and fabrics and the physical and chemical aspects of the actual processing of yarns and fabrics. The second part, consisting of sixteen chapters, covers in detail the chemical auxiliaries used in fabric processing (one chapter discusses water, an important wet processing raw material). There is some overlapping between the two parts. For example, Mosher, in chapter 5 (first part), discusses textile finishing and covers in some detail the chemistry of the products used; in chapter 17 (in the second part), Ackley discusses the chemistry of cationic finishing agents and discribes their use in finishing. Since the various chapters in the two parts have been prepared by different authors, this duplication is to be expected. It would be impossible to discuss textile finishing without discussing textile finishes. A discussion of textile finishes naturally requires some description of their use.

The book is up to date. The latest developments in dyeing and finishing techniques for Orlon, Dacron, Dynel, Vicara, Acrylan, and X-51 are included. Recently introduced textile specialties for wet processing and finishing are described.

Two errors have been noted by the reviewer. On page 299 mention is made "that certain non-ionics can be sulfonated to anionics, as in the sulfonation of Triton N-100 to Triton 720." Triton 720 is a sulfonate; it is an alkyl aryloxyethoxyethoxyethyl sodium sulfonate. It could not be obtained by the sulfonation of Triton N-100. Sulfonation of Triton N-100 would lead to the formation of an alkyl aryloxy(polyethoxy)ethyl *sulfate*. On page 314, again discussing two more Tritons, the author states that "Triton 770 is a sulfate and Triton W-30 is a sulfonate." Triton W-30 and Triton 770 are both sulfates.

The book is well written and easy to read, and each chapter has an excellent bibliography. The author index and the subject index are both adequate.

Textile Chemicals and Auxiliaries should prove useful as a source book for courses in textile chemistry

in textile schools and in industrial chemistry courses at other institutions. Textile technologists, chemists in dyeing and finishing plants, and laboratory personnel of chemical manufacturers will find the book informative and a useful reference tool.

Textile Untersuchungen. M. Nopitsch. Stuttgart, Germany, Konradin-Verlag, 1951. 322 + liv pages; 218 figures. Price, DM 32.50. (Available through Stechert-Hafner, Inc. New York.)

(Reviewed by Charles H. Lindsley, American Enka Corp., Enka, N. C.)

This book is written by the head of the Textile Chemistry Section of the Research Institute for Clothing Physiology, Schloss Hohenstein, Württemberg. The text is divided into two main sections of equal length: analytical procedures, and examples of faults or damage drawn from practical experience. In the first part, mechanical, chemical, and microscopical tests are described. The actual procedures are set apart by italic type from the accompanying commentary, and many marginal headings help in finding a particular method. In the second part, a large number of frequently occurring or particularly instructive examples of damaged yarns and fabrics are considered. Separate indexes for the two sections are given at the end.

Two sections of photographs are included, one showing testing apparatus and instruments (54 pictures) and the other giving 164 photomicrographs and drawings of fibers and fabrics. These are well chosen and reproduced, although there is little that is not available elsewhere.

Twenty-five pages at the beginning are devoted to descriptions of the principal fibers—natural, artificial, and synthetic. In a book of this kind it seems unnecessary to include manufacturing methods and names of producers (mainly German) of regenerated and synthetic textile materials.

The title is rather misleading, for the book does not deal with textile investigations in general; the center of interest is upon types of damage to textile materials and methods for determining the causes of damage in particular cases.

The book is well printed and bound. It contains much valuable information, and will no doubt prove useful to those concerned with the problems of textile testing.

Studies on the Microbiological Retting Process for the Preparation of a Hard Fiber, and Influence of this Process on the Fiber Properties. A. N. J. Heyn (in English). Amsterdam, Holland, Royal Netherlands Academy of Science, 1951. 59 pages; 8 plates. Price, $2.50. (A few copies are available from the author, at School of Textiles, Clemson Agricultural College, Clemson, S. C.)

This monograph describes fundamental studies on the preparation of coconut fiber in Indonesia which were carried out in 1937–1940 for the Netherlands Government in the East Indies. Publication of the report was delayed by the war.

It appears that methods of extracting the fiber from the husk employed in the principal coir-producing areas of India and Ceylon involves a long soaking process ranging up to one year. Very little was understood about the real nature of and the phenomena underlying this soaking process. The project, under the direction of Dr. Heyn, was directed towards the development of a suitable method for fiber production in Indonesia.

A study was made of the decomposition of pectins during the soaking process, and the presence of enzymes which decompose pectins was demonstrated. An actual isolation in pure culture was obtained of the active microorganism, which proved to be the anaerobic bacterium *Clostridium felsineum*, earlier described by Carbone for the retting of hemp in Italy. A discussion of retting organisms in general is given in connection with these findings. It is concluded that the soaking process is essentially a retting process. The conditions for producing a fiber of superior quality were determined, and plants for its preparation were established. In this monograph only the underlying research is reported, with no details of the retting process as finally developed being disclosed.

In the second part of the monograph the color of the fiber is studied, which is of first importance for its commercial value. The color was found to be due to phlobaphenes formed from tannic substances by a photochemical process. The content of these substances in fiber and husk during the retting process was studied, and the relationship between the application of a suitable retting process and a light color of the fiber established.

Considerable data are included in the report, which is illustrated by photographs and photomicrographs. An extensive bibliography is included.

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DRUSPIN WL	13	6	36	Fair	4th
An Amine Condensate plus Phosphates	44	130	Non-applicable	Poor	—
Self-Scouring Synthetic Wool Oil	90	140	Non-applicable	Poor	—
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Blank	85	135	Non-applicable	Poor	—

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